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(54) Title: PROCESS FOR THE CO-OLIGOMERISATION OF ETHYLENE AND ALPHA OLEFINS

(57) Abstract: A process for production of higher linear alpha olefins and/or alkyl-branched alpha olefins, which comprises the co-oligomerisation of one or more alpha olefins with ethylene in the presence of a metal catalyst system employing one or more bis-aryliminepyridine MX_n complexes and/or one or more [bis-aryliminepyridine $MY_p.L_b^+$] $[NC^-]_q$ complexes; and said process is carried out at an ethylene pressure of less than 2.5 MPa.

PROCESS FOR THE CO-OLIGOMERISATION OF ETHYLENE AND ALPHA OLEFINS

The present invention relates to a process for the co-oligomerisation of ethylene and alpha olefins and to product compositions produced therein.

Various processes are known for the production of higher linear alpha olefins (for example D. Vogt, *Oligomerisation of ethylene to higher α-olefins* in *Applied Homogeneous Catalysis with Organometallic Compounds* Ed. B. Cornils, W.A. Herrmann Vol. 1, Ch. 2.3.1.3, page 245, VCH 1996).

These commercial processes afford either a Poisson or Schulz-Flory oligomer product distribution. In order to obtain a Poisson distribution, no chain termination must take place during oligomerisation. However, in contrast, in a Schulz-Flory process, chain termination does occur and is independent of chain length. The Ni-catalysed ethylene oligomerisation step of the Shell Higher Olefins Process (SHOP) is a typical example of a Schulz-Flory process.

In a Schulz-Flory process, a wide range of oligomers are typically made in which the fraction of each olefin can be determined by calculation on the basis of the so-called K-factor. The K-factor, which is indicative of the relative proportions of the product olefins, is the molar ratio of $[C_{n+2}]/[C_n]$ calculated from the slope of the graph of log $[C_n$ mol%] versus n, where n is the number of carbon atoms in a particular product olefin. The K-factor is by definition the same for each n. By

ligand variation and adjustment of reaction parameters, the K-factor can be adjusted to higher or lower values. In this way, the process can be operated to produce a product slate with an optimised economic benefit.

In WO-A-99/02472, there are disclosed novel iron-based ethylene oligomerisation catalysts that show high activity and high selectivity towards linear alpha olefins. The catalysts are based on iron complexes of a selected 2,6-pyridinedicarboxaldehyde bisimine or a selected 2,6-diacylpyridine bisimine.

In the present invention the term "bis-(aryliminoalkyl)pyridine", or in short, "bis-arylimine pyridine" is used to describe both classes of ligands.

In our co-pending European Patent Application No. 00301036.0 such systems are further improved, in particular with respect to the oligomer product distribution.

The bis-arylimine pyridine-$FeCl_2$ based catalysts have been shown to be highly reactive towards ethylene but the reactivity towards other olefins such as propylene or higher alpha olefins has been found to be orders of magnitude lower.

B.L. Small and M. Brookhart disclosed in J. Am. Chem. Soc. 1998, 120, 7143-7144, that the oligomerisation of ethylene at a pressure of 400 psig (2.76 MPa) in the presence of a 50:50 volume ratio of 1-pentene to toluene as solvent and a bis-arylimine pyridine-$FeCl_2$ based catalyst gave only ca. 3 mol. % of odd carbon number oligomers, thereby demonstrating the very high selectivity of such a catalyst for insertion of ethylene relative to alpha olefins.

Further experiments therein with a different bis-aryliminepyridine-$FeCl_2$ catalyst showed even greater selectivity towards insertion of ethylene relative to the insertion of alpha olefins, with only traces (< 1 %) of odd oligomers produced.

The high selectivity of these catalysts towards ethylene was confirmed by the studies of V.C. Gibson et al., as disclosed in Chem. Eur. J. 2000, 6, 2221-2231.

Therefore, not surprisingly, the application of such catalyst systems has focused on products and processes with ethylene as feedstock and with preferentially no or little branching in products, for example, production of linear alpha olefins.

For an oligomerisation process, the basic reaction steps of chain growth and chain termination are balanced in such a way that products with a limited molecular weight are formed, that is to say, the amount of products with high molecular weights is minimal.

In a simplified view, one may consider chain growth to occur by ethylene insertion in a metal-hydrogen bond (for the first monomer affording a metal-ethyl species) and metal-carbon bonds (for the second monomer and more).

It is a general phenomenon that other olefins besides ethylene may participate in reactions with metal-hydrogen or metal-carbon bonds. In particular, mono-substituted alpha olefins are reactive. The outcome of the reaction is influenced by the structures of the active intermediates, the way the alpha olefins react with these, and the way the generated metal-alkyl compounds react further.

In ethylene oligomerisation reactions, the formation of by-products such as branched olefins, 2,2-substituted alpha olefins (vinylidene-type olefins), and internal olefins can be readily explained by these intermediates.

It will be evident that in view of the alpha olefin oligomer distribution generated in ethylene oligomerisations, a wide array of by-products may form leading to loss of product quality and waste of valuable ethylene feed. However, catalysts which combine a particular reactivity towards alpha-olefins with ethylene oligomerisation capability would be of great value to generate new technologies for producing alpha olefins from alternative feedstocks or for (mixtures of) alpha olefin products with particular structures designed in order to exhibit desirable properties.

For example, producing 1-hexene, 1-octene, or 1-decene by homologation of 1-butene with ethylene can be envisioned by systems which after chain termination start by "1,2"-insertion of 1-butene in the metal-hydrogen bond (formed after chain termination) but which subsequently do not react extensively with any other olefin but ethylene before termination. In this way, cheaply available refinery 1-butene can be converted to high-valued alpha olefins.

Another interesting possibility is the formation of alkyl-branched alpha olefins with a well-defined branching pattern as a result of catalyst properties and reaction conditions. For example, methyl-branched alpha olefins may be obtained by systems which after chain termination preferentially start with "2,1"-insertion of an olefin into the metal-hydrogen bond and which subsequently do not react extensively with any other olefin than ethylene before termination.

In the present invention by "methyl-branched alpha olefin" is meant an olefin formed by "2,1"-insertion of an alpha olefin formally into the metal-hydrogen bond of the system and which system subsequently does not react extensively with any other olefin than ethylene before

termination. This "2,1"-insertion of an olefin into the metal-hydrogen bond may alternatively be explained by chain termination by hydrogen transfer to a co-ordinated olefin providing a metal-(2-alkyl) species as the start for the oligomerisation process. For sake of simplicity the first-mentioned mechanism will be adhered to in the further text.

The formation of C_8-C_{16} methyl-branched alpha-olefins is of great economic value as they may serve as feedstock for the alkylation of benzene, and thereby providing starting materials for high-solubility alkylbenzene sulphonate surfactants, and as feedstock for hydroformylation processes yielding high-solubility detergent alcohols and derivatives.

Moreover, if, for example, 1-decene were to be used as the "solvent" for ethylene (co-)oligomerisation, one single process would yield linear 1-alkenes in the C_4-C_{10} range as well as linear and/or branched 1-alkenes in the range $>C_{12}$.

Besides specific methyl-branching, products with specific ethyl-branching are of economical interest. Preference for ethyl-branching can be envisaged to be endorsed in catalyst systems in which the chain transfer reaction preferably takes place to ethylene monomer. In the resulting metal-ethyl species, chain growth may occur either by incorporation of additional ethylene or a different olefinic co-monomer.

In the present invention by "ethyl-branched alpha olefin" is meant an olefin formed by "1,2"-insertion of an alpha olefin formally into the metal-ethyl bond of the system and which system subsequently does not react extensively with any other olefin than ethylene before termination.

Ascertaining whether the proposed reactions and formation of the desired molecular structures described above have taken place during ethylene oligomerisation, is thwarted by the fact that the same product may be generated by more than one reaction path.

For example, linear alpha olefins may be formed not only by pure ethylene oligomerisation but also homologation of a smaller "1,2"-inserted alpha olefin with ethylene.

A more detailed insight into products and reaction steps may be obtained from co-oligomerisation experiments in which the co-monomer is an odd-numbered alpha olefin. Ethylene oligomerisations which take place in the presence of odd-numbered alpha olefins will give information on incorporation of olefins in products by comparison and characterisation of odd- and even-numbered products. For example, ethylene oligomerisation in the presence of 1-heptene may afford the usual C_{2n} alpha olefins as well as the linear odd alpha olefins starting from 1-nonene, C_9. The ratio of the amounts of odd and even linear olefins provides a measure of the relative reactivities of ethylene and alpha olefins in the first step of the chain growth in experiments.

Important information on (by-)product structures in ethylene oligomerisations may be obtained by performing the reaction in the presence of a large excess of a particular alpha olefin, for example, a co-oligomerisation. This has the effect of simplifying the normally obtained oligomer distribution by a singular olefin of the same reactivity. As a result (by-)product formation due to incorporation of produced alpha olefins based on the single co-monomer and yield well-defined structures is now apparent.

These structures are relatively easy to characterise even if present in small amounts by comparison of ^{1}H- and ^{13}C-NMR spectra of samples containing different levels of (by-)products. Characteristic NMR resonances for unsaturated end-groups in alpha-olefins, 2,2-disubstituted alpha olefins (vinylidene type olefins), single methyl and ethyl groups along an aliphatic chain are known in the literature and can be used.

The presence of 2,2-disubstituted alpha olefins can be explained by "1,2"-insertion of an alpha olefin into the metal carbon bond of a growing chain, followed by chain termination (β-H elimination). The occurrence of a distribution of methyl-branched alpha olefins is in line with a chain growth process in which the first step of the reaction involves, a "2,1"-insertion of the co-monomer formally in a metal-hydride affording a metal-(2-alkyl) intermediate which undergoes subsequent ethylene oligomerisations. In a similar fashion, the occurrence of a distribution of ethyl-branched alpha olefins can be explained by assuming that chain termination occurs by hydrogen transfer to a co-ordinated ethylene monomer providing a metal-ethyl species as the start for the oligomerisation process in which the first step is a "1,2"-insertion of an alpha olefin into this metal-ethyl bond, affording a metal-(3-alkyl) intermediate which undergoes subsequent ethylene oligomerisations. Of course, the type of by-products observed should show similar patterns for odd- and even-numbered alpha olefin co-monomer.

It has now been surprisingly found that by tuning reaction conditions, in particular using suitable olefins at appropriate concentrations in an ethylene co-oligomerisation reaction and the specific bis-

aryliminepyridine metal catalyst systems used therein, the formation of linear alpha olefins by ethylene-homologation of smaller linear alpha olefins and the formation of alkyl-branched, in particular methyl-branched and/or ethyl-branched, alpha olefins can be greatly enhanced.

By "alkyl-branched alpha olefin" in the present invention is meant preferably "methyl-branched alpha olefin", "ethyl-branched alpha olefin" or a combination thereof.

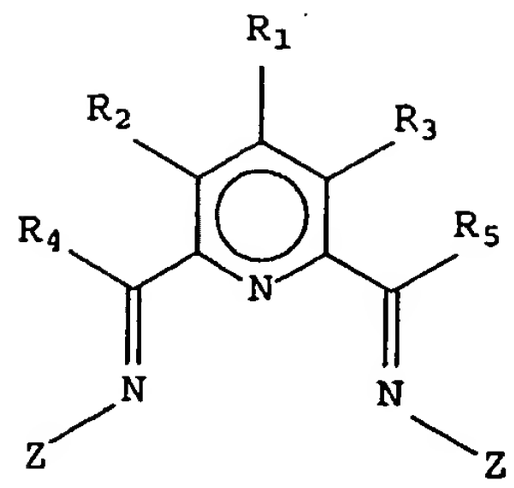
It will be appreciated that whilst the alkyl-branched alpha olefins of the present invention may be formed by the tentative mechanisms described above, it is not precluded that said olefins may be formed by an alternative reaction mechanism.

The general structure of "alkyl-branched alpha olefins" is given in the formula below,

$$C=C[-C-C]_n[-C]_m(R_{16})-R$$

wherein R_{16} = methyl; n = 0, 1, 2, etc.; m = 1; R = optionally substituted hydrocarbyl, preferably comprising 1 to 30 carbon atoms, or R_{16} = ethyl; n = 0, 1, 2, etc.; m = 0; R = optionally substituted hydrocarbyl, preferably comprising 1 to 30 carbon atoms.

The present invention provides a process for production of higher linear alpha olefins and/or alkyl-branched alpha olefins, which comprises the co-oligomerisation of one or more alpha olefins with ethylene in the presence of a metal catalyst system employing one or more bis-aryliminepyridine MX_a complexes and/or one or more [bis-aryliminepyridine $MY_p.L_b^+$] $[NC^-]_q$ complexes, said bis-aryliminepyridine complexes comprising a ligand of the formula,

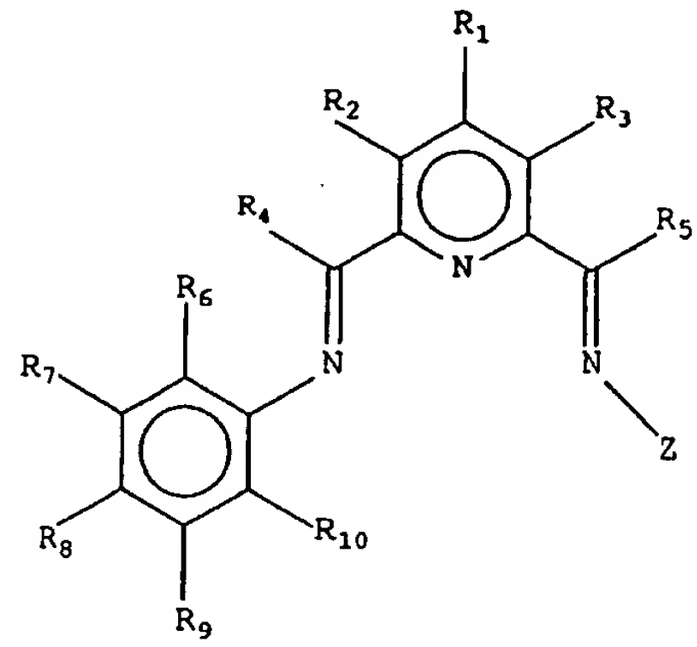


(I)

wherein M is a metal atom selected from Fe or Co; a is 2 or 3; X is halide, optionally substituted hydrocarbyl, alkoxide, amide, or hydride; Y is a ligand which may insert an olefin; NC^- is a non-coordinating anion; p+q is 2 or 3, matching the formal oxidation of said metal atom; L is a neutral Lewis donor molecule; b = 0, 1, or 2; R_1-R_5 are each, independently, hydrogen, optionally substituted hydrocarbyl, an inert functional group, or any two of R_1-R_3 vicinal to one another taken together may form a ring; each Z, which may be identical or different, is an optionally substituted aromatic hydrocarbon ring; an optionally substituted polyaromatic hydrocarbon moiety; an optionally substituted heterohydrocarbyl moiety; or an optionally substituted aromatic hydrocarbon ring in combination with a metal, said optionally substituted aromatic hydrocarbon ring being π-co-ordinated to the metal;
and said process is carried out at an ethylene pressure of less than 2.5 MPa.

In a preferred embodiment of the present invention, there is provided a process for production of higher linear alpha olefins and/or alkyl-branched alpha olefins, which comprises the co-oligomerisation of one or more

alpha olefins with ethylene in the presence of a metal catalyst system employing one or more bis-aryliminepyridine MX_a complexes and/or one or more [bis-aryliminepyridine $MY_p.L_b^+$] $[NC^-]_q$ complexes, said bis-aryliminepyridine complexes comprising a ligand of the formula,

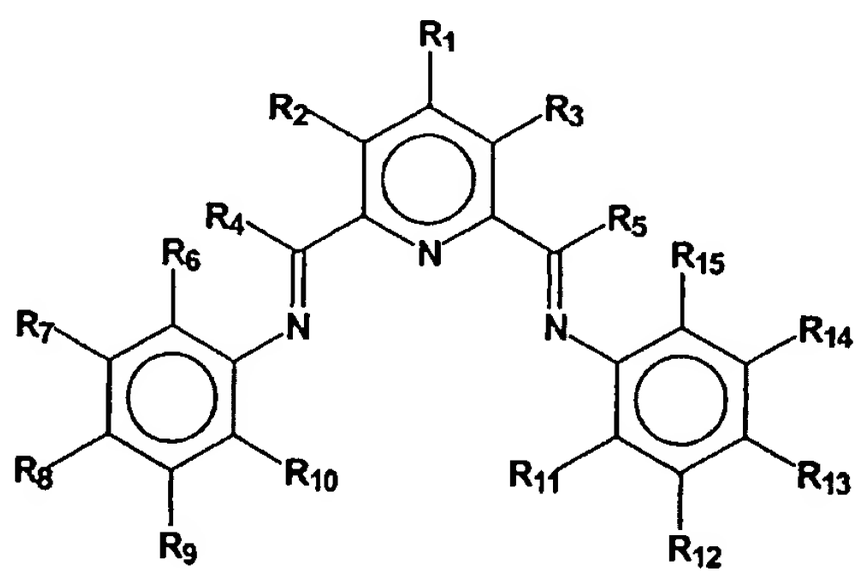


(II)

wherein M is a metal atom selected from Fe or Co; a is 2 or 3; X is halide, optionally substituted hydrocarbyl, alkoxide, amide, or hydride; Y is a ligand which may insert an olefin; NC^- is a non-coordinating anion; p+q is 2 or 3, matching the formal oxidation of said metal atom; L is a neutral Lewis donor molecule; b = 0, 1, or 2; R_1-R_{10} are each, independently, hydrogen, optionally substituted hydrocarbyl, an inert functional group, or any two of R_1-R_3, R_6-R_{10} vicinal to one another taken together may form a ring; R_6 may be taken together with R_4 to form a ring; R_{10} may be taken together with R_4 to form a ring; Z is an optionally substituted aromatic hydrocarbon ring; an optionally substituted polyaromatic

hydrocarbon moiety; an optionally substituted heterohydrocarbyl moiety; or an optionally substituted aromatic hydrocarbon ring in combination with a metal, said optionally substituted aromatic hydrocarbon ring being π-co-ordinated to the metal; and said process is carried out at an ethylene pressure of less than 2.5 MPa.

In a preferred embodiment of the present invention, there is provided a process for production of higher linear alpha olefins and/or alkyl-branched alpha olefins, which comprises the co-oligomerisation of one or more alpha olefins with ethylene in the presence of a metal catalyst system employing one or more bis-aryliminepyridine MX_a complexes and/or one or more [bis-aryliminepyridine $MY_p.L_b^+$] $[NC^-]_q$ complexes, said bis-aryliminepyridine complexes comprising a ligand of the formula,



(III)

wherein M is a metal atom selected from Fe or Co; a is 2 or 3; X is halide, optionally substituted hydrocarbyl, alkoxide, amide, or hydride; Y is a ligand which may insert an olefin; NC^- is a non-coordinating anion; p+q is 2 or 3, matching the formal oxidation of said metal atom;

L is a neutral Lewis donor molecule; b = 0, 1, or 2; R_1-R_5, R_7-R_9 and R_{12}-R_{14} are each, independently, hydrogen, optionally substituted hydrocarbyl, an inert functional group, or any two of R_1-R_3, R_7-R_9 and R_{12}-R_{14} vicinal to one another taken together may form a ring; R_6 is hydrogen, optionally substituted hydrocarbyl, an inert functional group, or taken together with R_7 or R_4 to form a ring; R_{10} is hydrogen, optionally substituted hydrocarbyl, an inert functional group, or taken together with R_9 or R_4 to form a ring; R_{11} is hydrogen, optionally substituted hydrocarbyl, an inert functional group, or taken together with R_5 or R_{12} to form a ring; and R_{15} is hydrogen, optionally substituted hydrocarbyl, an inert functional group, or taken together with R_5 or R_{14} to form a ring; and said process is carried out and at an ethylene pressure of less than 2.5 MPa.

In one embodiment, of the present invention the metal catalyst system used employs one or more bis-aryliminepyridine MX_a complexes and a second compound which is capable of transferring an optionally substituted hydrocarbyl or hydride group to a metal atom M selected from Fe or Co, and which is also capable of abstracting an X^- group from said metal atom.

In another embodiment, of the present invention the metal catalyst system used employs one or more bis-aryliminepyridine MX_a complexes, a second compound which is capable of transferring an optionally substituted hydrocarbyl or hydride group to a metal atom M selected

from Fe or Co, and a third compound which is capable of abstracting an X^- group from said metal atom.

In the present invention certain terms are used as follows:

By "higher" in higher linear alpha olefins and higher alkyl-branched alpha olefins is meant molecules containing from 4 to 30 carbon atoms.

Examples of optionally substituted aromatic hydrocarbon rings and optionally substituted polyaromatic hydrocarbon moieties include phenyl, naphthyl, anthracenyl, phenanthracenyl, and the like and substituted derivatives thereof.

The term "optionally substituted aromatic hydrocarbon ring in combination with a metal, said optionally substituted aromatic hydrocarbon ring being π-co-ordinated to the metal" includes metallocene moieties and sandwich and metal-arene complexes. Thus, it will be appreciated by the person skilled in the art that, optionally, the metal may be additionally π-co-ordinated to a further optionally substituted aromatic hydrocarbon ring, which may be different to the optionally substituted aromatic hydrocarbon ring in Z which is directly bonded to the imine nitrogen atom and/or co-ordinated to other ligands commonly known in the art. It will be further appreciated that the optionally substituted aromatic hydrocarbon ring in Z which is directly bonded to the imine nitrogen atom and which is also π-co-ordinated to the metal, may comprise one or more heteroatoms in the ring, i.e., such that said optionally substituted aromatic hydrocarbon ring is an optionally substituted aromatic heterocyclic group. Similarly, the further optionally substituted aryl group that the metal may additionally be π-co-ordinated to,

may comprise one or more heteroatoms in the ring. Said metal atom may conveniently be iron, cobalt, nickel, chromium, titanium and vanadium. Examples of such moieties include the radical derived from ferrocene, cobaltocene, nickelocene, chromocene, titanocene, vanadocene, bis-π-arene vanadium complex, mono-π-arene chromium tricarbonyl complex and similar heteroarene metal complexes, i.e. bis- or mono-π-thiene or pyrrole iron or chromium complexes.

The term "heterohydrocarbyl" refers to a hydrocarbyl group, additionally containing one or more heteroatoms. Said heteroatoms are preferably bonded to at least two carbons in the heterohydrocarbyl group. Preferred heteroatoms are nitrogen, oxygen and sulphur.

Said heterohydrocarbyl group may be an optionally substituted aromatic heterocyclic moiety; an optionally substituted polyaromatic heterocyclic moiety; an optionally substituted aliphatic heterocyclic moiety; or an optionally substituted aliphatic heterohydrocarbyl moiety.

Examples of heterohydrocarbyl groups include 1-pyrrolyl, 2-pyrrolyl, 3-pyrrolyl, furyl, thienyl, indenyl, imidazolyl, triazolyl, oxazolyl, isoxazolyl, carbazolyl, thiazolyl, benzothiazolyl, thiadiazolyl, pyrimidinyl, pyridyl, pyridazinyl, and the like and substituted derivatives thereof.

Hydrocarbyl group: a group containing only carbon and hydrogen. Unless otherwise stated, the number of carbon atoms is preferably between 1 and 30.

In the present invention, the phrase "optionally substituted hydrocarbyl" is used to describe hydrocarbyl groups optionally containing one or more "inert" heteroatom-containing functional groups. By "inert" is

meant that the functional groups do not interfere to any substantial degree with the co-oligomerisation process. Non-limiting examples of such inert groups are fluoride, chloride, silanes, stannanes, ethers and amines with adequate steric shielding, all well-known to those skilled in the art. Said optionally substituted hydrocarbyl may include primary, secondary and tertiary carbon atom groups of the nature described below.

Inert functional group: a group other than optionally substituted hydrocarbyl which is inert under the process conditions. By "inert" is meant that the functional group does not interfere to any substantial degree with the co-oligomerisation process. Examples of inert functional groups include halide, ethers, and amines, in particular tertiary amines.

Primary carbon atom group: a $-CH_2-R$ group wherein R may be hydrogen, a optionally substituted hydrocarbyl, inert functional group. Examples of primary carbon atom groups include $-CH_3$, $-C_2H_5$, $-CH_2Cl$, $-CH_2OCH_3$, $-CH_2N(C_2H_5)_2$, $-CH_2Ph$.

Secondary carbon atom group: a $-CH-R_2$ group wherein R may be optionally substituted hydrocarbyl, inert functional group. Examples of secondary carbon atom groups include $-CH(CH_3)_2$, $-CHCl_2$, $-CHPh_2$, $-CH=CH_2$, cyclohexyl.

Tertiary carbon atom group: a $-C-R_3$ group wherein R may be optionally substituted hydrocarbyl, inert functional group. Examples of tertiary carbon atom groups include $-C(CH_3)_3$, $-CCl_3$, $-C\equiv CPh$, 1-Adamantyl, $-C(CH_3)_2(OCH_3)$.

By a "ligand which may insert an olefin" is meant a ligand which is coordinated to a metal ion into which bond an ethylene molecule or an alpha-olefin may be inserted to initiate or propagate a co-oligomerisation reaction. In [bis-aryliminepyridine $MY_p.L_b^+][NC^-]_q$ complexes according to the present invention, Y may be hydride, alkyl or any other anionic ligand which may insert an olefin.

By "non-coordinating anion" is meant an anion which does not substantially coordinate to the metal atom M. Non-coordinating anions (NC^-) that may be suitably employed include bulky anions such as tetrakis [3,5-bis(trifluoromethyl)phenyl]borate (BAF^-), $(C_6F_5)_4B^-$, and anions of alkylaluminium compounds including R_3AlX^-, R_2AlClX^-, $RAlCl_2X^-$, and "$RAlOX^-$", wherein R is hydrogen, optionally substituted hydrocarbyl or an inert functional group, and X is halide, alkoxide or oxygen.

It will be appreciated by those skilled in the art that within the boundary conditions hereinbefore described, substituents R_1-R_{15} may be readily selected to optimise the performance of the catalyst system and its economical application.

Substituents R_1-R_5, R_7-R_9, R_{12}-R_{14} may independently be linked together and form cyclic structures.

In one embodiment of the present invention, R_1-R_5, R_7-R_9 and R_{12}-R_{14} are each, independently, hydrogen, optionally substituted hydrocarbyl, an inert functional group, or any two of R_1-R_3, R_7-R_9 and R_{12}-R_{14} vicinal to one another taken together may form a ring; R_6 is a

primary carbon group, a secondary carbon group or a tertiary carbon group; and provided that:

when R_6 is a primary carbon group none, one or two of R_{10}, R_{11} and R_{15} are primary carbon groups, and the remainder of R_{10}, R_{11} and R_{15} are hydrogen;

when R_6 is a secondary carbon group none or one of R_{10}, R_{11} and R_{15} is a primary carbon group or a secondary carbon group and the remainder of R_{10}, R_{11} and R_{15} are hydrogen;

when R_6 is a tertiary carbon group all of R_{10}, R_{11} and R_{15} are hydrogen; and

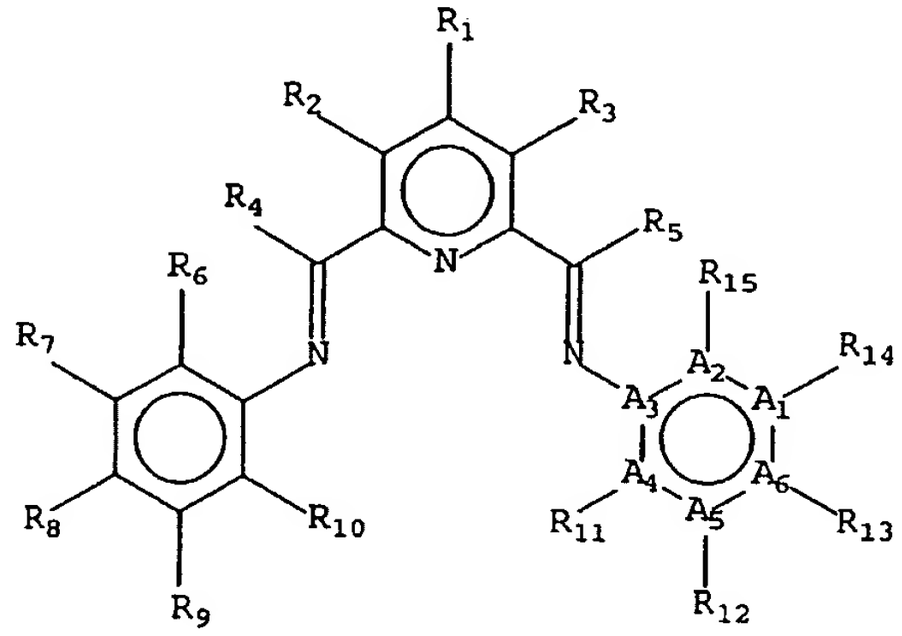
any two of R_6, R_7, R_8, R_9, R_{10}, R_{11}, R_{12}, R_{13}, R_{14} and R_{15} vicinal to one another, taken together may form a ring.

In another embodiment of the present invention, R_1-R_5, R_7-R_9 and R_{12}-R_{14} are each, independently, hydrogen, optionally substituted hydrocarbyl, an inert functional group, or any two of R_1-R_3, R_7-R_9 and R_{12}-R_{14} vicinal to one another taken together may form a ring; R_6 is hydrogen, optionally substituted hydrocarbyl, an inert functional group, or taken together with R_7 or R_4 to form a ring; R_{10} is hydrogen, optionally substituted hydrocarbyl, an inert functional group, or taken together with R_9 or R_4 to form a ring; R_{11} and R_{15} are, independently, hydrogen or an inert functional group.

In a further embodiment of the present invention, R_1-R_5, R_7-R_9 and R_{12}-R_{14} are each, independently, hydrogen,

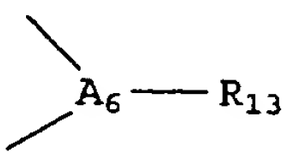
optionally substituted hydrocarbyl, an inert functional group, or any two of R_1-R_3, R_7-R_9 and R_{12}-R_{14} vicinal to one another taken together may form a ring; R_6, R_{10}, R_{11} and R_{15} are identical and are each selected from fluorine or chlorine.

In another embodiment of the process of the present invention, the bis-arylimine pyridine complexes employed therein comprise a ligand of formula (IV),



(IV)

wherein A_1-A_6 are each, independently, carbon, nitrogen, oxygen, or sulphur; the atom group



may be optionally absent such that A_1 is directly bonded to A_5; and R_1-R_{12}, R_{14}-R_{15} and, if present, R_{13}, are each, independently, hydrogen, optionally substituted hydrocarbyl, an inert functional group, or any two of R_1-R_{15} vicinal to one another taken together may form a ring; with the proviso that when A_1-A_5, and A_6 if

present, are all carbon, said atoms constitute the cyclopentadienyl or aryl part of a π-co-ordinated metal.

In a preferred embodiment of the present invention, in formula (IV), R_1-R_3, R_7-R_9, R_{12}, R_{14} and, if present, R_{13}, are each, independently, hydrogen, optionally substituted hydrocarbyl, an inert functional group, or any two of R_1-R_3, R_7-R_9, R_{12}-R_{14} vicinal to one another taken together may form a ring; and

a) R_6 is an inert functional group or an optionally substituted hydrocarbyl, and R_{10}, R_{11}, and R_{15} are, independently, hydrogen or halide; or

b) R_{11} is an inert functional group or an optionally substituted hydrocarbyl, and R_6, R_{10}, and R_{15} are, independently, hydrogen or halide; or

c) R_6 and R_{10} are each, independently, inert functional group or a primary or secondary carbon atom group, provided that R_6 and R_{10} are not both a secondary carbon atom group and R_{11} and R_{15} are, independently, hydrogen or halide; or

d) R_{11} and R_{15} are each, independently, inert functional group or a primary or secondary carbon atom group, provided that R_{11} and R_{15} are not both a secondary carbon atom group and R_6 and R_{10} are, independently, hydrogen or halide; or

e) R_6 is taken together with R_7 to form a ring, R_{10} is a primary carbon atom group, an inert functional group, or hydrogen and R_{11} and R_{15} are, independently, hydrogen or halide; or

f) R_{11} is taken together with R_{12} to form a ring, R_{15} is a primary carbon atom group, an inert functional

group, or hydrogen and R_6 and R_{10} are, independently, hydrogen or halide; or

g) R_6 and R_{10} are taken together with R_7 and R_9, respectively, to form rings and R_{11} and R_{15} are, independently, hydrogen or halide; or

h) R_{11} and R_{15} are taken together with R_{12} and R_{14}, respectively, to form rings and R_6 and R_{10} are, independently, hydrogen or halide.

In formula (IV), substituents R_{1-15}, if present, may independently be linked together and form cyclic structures. Examples of such structures include the linking of, for example, R_6 with R_7, to form the basic naphthyl skeleton or a tetrahydronaphthyl unit.

Furthermore, it will be readily appreciated by any person who has mastered the basic principles of homogeneous catalysis, that in all of the above-mentioned ligands for use in the bis-arylimine pyridine complexes employed in the process of the present invention, substituent variations of R_{1-5}, R_{7-9}, and R_{12-14}, if present, may be selected so as to enhance other desirable properties of catalyst precursors and catalyst systems such as solubility in non-polar solvents or extending the range of suitable starting materials in their syntheses.

Preferred embodiments of the present invention employ ligands according to formula (I) and derivatives thereof, in which the following R groups appear:

R_1-R_3 are hydrogen; and/or R_4 and R_5 are methyl, hydrogen, benzyl or phenyl, preferably methyl, phenyl or hydrogen.

Preferred embodiments of the present invention employ ligands according to formulae (I), (II), (III) and (IV),

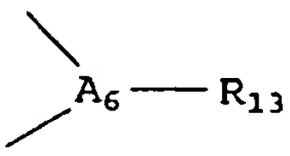
and derivatives thereof, in which the following R groups appear:

R_1-R_3 are hydrogen; and/or R_4 and R_5 are methyl, hydrogen, benzyl or phenyl, preferably methyl, phenyl or hydrogen.

Preferred embodiments are ligands according to (IV) and derivatives thereof, in which the following R groups appear:

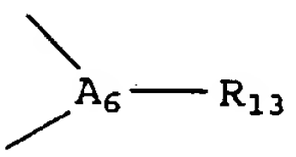
R_1-R_3 are hydrogen; and/or

R_4 and R_5 are methyl, hydrogen or phenyl, preferably methyl; and/or



is absent and A_1-A_5 are carbon atoms, thereby constituting the cyclopentadienylide part of a ferrocenyl moiety; or

A_3 is a nitrogen atom,



is absent and A_1, A_2, A_4, A_5 are carbon atoms, thereby constituting a 1-pyrrolyl ring; and/or

Combinations of *ortho*-substituents in which R_6 is methyl, ethyl, *iso*-propyl, phenyl, *tertiary*-butyl, or linked to R_7 to form a naphthyl skeleton; R_{10} is hydrogen, fluoride, or chloride; R_{11} and R_{15} are independently, hydrogen, fluoride or chloride and/or

Combinations of *ortho*-substituents in which R_6 and R_{10} are, independently, methyl, ethyl, or linked to R_7 and R_9, respectively, to form an anthracene skeleton, preferably methyl; R_{11} and R_{15} are, independently, hydrogen, fluoride or chloride.

It is particularly preferred that in formula (IV) R_{11} and R_{15} are, independently, hydrogen or fluoride.

Preferred ligands include:-

a ligand of formula (II), wherein R_1-R_3 are hydrogen; R_4 and R_5 are methyl; R_6, R_8, R_{10} are methyl; R_7, R_9 are hydrogen and Z is 1-pyrrolyl;

a ligand of formula (II), wherein R_1-R_3 are hydrogen; R_4 and R_5 are methyl; R_6, R_8, R_{10} are methyl; R_7 and R_9 are hydrogen and Z is ferrocenyl;

a ligand of formula (III), wherein R_1-R_3 are hydrogen; R_4 and R_5 are methyl; R_6, R_8, and R_{10} are methyl; R_7 and R_9 are hydrogen; R_{11} and R_{15} are hydrogen; R_{12} and R_{14} are hydrogen; and R_{13} is tert-butyl;

a ligand of formula (III), wherein R_1-R_3 are hydrogen; R_4 and R_5 are methyl; R_6 and R_7 are taken together to form a six-membered aromatic ring; R_8 and R_{10} are hydrogen; R_9 is hydrogen; R_{11} and R_{15} are hydrogen; R_{12} and R_{14} are hydrogen; and R_{13} is tert-butyl;

a ligand of formula (III), wherein R_1-R_3 are hydrogen; R_4 and R_5 are methyl; R_6 is tert-butyl; R_7-R_{10} are hydrogen; R_{11} and R_{15} are hydrogen; R_{12} and R_{14} are hydrogen; and R_{13} is tert-butyl;

a ligand of formula (III), wherein R_1-R_3 are hydrogen; R_4 and R_5 are methyl; R_6, R_8 and R_{10} are methyl; R_7 and R_9 are hydrogen; R_{11} is fluorine; and R_{12}-R_{15} are hydrogen;

a ligand of formula (III), wherein R_1-R_3 are hydrogen; R_4 and R_5 are methyl; R_6 is tert-butyl; R_7-R_{10} are hydrogen; R_{11}, R_{13} and R_{15} are hydrogen; and R_{12} and R_{14} are methyl;

a ligand of formula (III), wherein R_1-R_3 are hydrogen; R_4 and R_5 are methyl; R_6 and R_{10} are fluorine; R_7-R_9 are hydrogen; R_{12} and R_{15} are methyl; and R_{11}, R_{13} and R_{14} are hydrogen; and

a ligand of formula (III), wherein R_1-R_3 are hydrogen; R_4 and R_5 are methyl; R_7-R_9 and R_{12}-R_{14} are hydrogen; and R_6, R_{10}, R_{11} and R_{15} are fluorine.

a ligand of formula (III), wherein R_1-R_3 are hydrogen; R_4 and R_5 are methyl; R_7-R_{10} are hydrogen; R_6 is methyl; R_{11}-R_{14} are hydrogen; and R_{15} is methyl.

In the bis-aryliminepyridine MX_a complex, X may conveniently be halide, preferably chloride.

In a preferred embodiment of the bis-aryliminepyridine MX_a complex, metal atom M is Fe and a is 2. In another preferred embodiment, metal atom M is Fe and a is 3.

Compounds which are capable of transferring an optionally substituted hydrocarbyl or hydride group to metal atom M, and which are also capable of abstracting an X^- group from metal atom M include alkylaluminium compounds such as alkylaluminoxane and alkylaluminium halides. A preferred compound is methylaluminoxane.

Compounds which are capable of transferring an optionally substituted hydrocarbyl or hydride group to metal atom M include alkylaluminium compounds including

alkyl aluminoxanes, alkyl lithium compounds, Grignards, alkyl tin and alkyl zinc compounds.

Compounds which are capable of abstracting an X^- group from metal atom M include strong neutral Lewis acids such as SbF_5, BF_3 and Ar_3B, wherein Ar is a strong electron-withdrawing aryl group such as C_6F_5 or 3,5-$(CF_3)_2C_6H_3$.

A neutral Lewis donor molecule is a compound which may suitably act as a Lewis base, such as ethers, amines, sulphides and organic nitriles.

The use of donor molecules (Lewis Bases) such as triethylamine or 2,6-di-tert-butylpyridine, and/or acceptor molecules (Lewis Acids) such as diethylzinc, may have a positive influence on the selectivity of the ethylene co-oligomerisation process.

Furthermore, Lewis acids such as tri-*iso*-butylaluminium (TIBA) may enhance the continuous operation of the Fe- or Co- catalysed ethylene co-oligomerisation by enabling the preparation of stable and clear catalyst precursor solutions, in contrast to MAO activated and solubilised catalyst precursor solutions, which may become turbid upon standing.

In the [bis-aryliminepyridine $MY_p.L_n^+][NC^-]_q$ complex according to the present invention, L may be a neutral Lewis donor molecule capable of being displaced by ethylene, or a vacant coordination site.

In the [bis-aryliminepyridine $MY_p.L_n^+][NC^-]_q$ complex according to the present invention, metal atom M is preferably Fe and the formal oxidation state of said metal atom may be 2 or 3.

The catalyst system may be formed by mixing together the complex and optional additional compounds, preferably in a solvent such as toluene or isooctane.

The mole ratio of MX_n complex, second compound, and optionally third compound is not limited in the present invention.

It is possible to enhance the flexibility of an co-oligomerisation reaction by employing a mixture of one or more catalyst systems according to the present invention.

Such a quantity of the catalyst system is usually employed in the co-oligomerisation reaction mixture so as to contain from 10^{-4} to 10^{-9} gram atom, of metal atom M, in particular of Fe [II] or [III] metal, per mole of ethylene and/or alpha olefin to be reacted.

The co-oligomerisation reaction may be conveniently conducted over a range of temperatures from -100°C to 300°C, preferably in the range of from 0°C to 200°C, and more preferably in the range of from 50°C to 150°C.

The co-oligomerisation reaction is preferably carried out at an ethylene pressure of less than 2.0 MPa (20 bar(a)), and more preferably at an ethylene pressure between 0.1 MPa (1 bar(a)) and 1.6 MPa (16 bar(a)).

Alpha olefin co-monomer is generally present in a concentration of greater than 1 $mol.l^{-1}$, preferably in a concentration of greater than 2.5 $mol.l^{-1}$, and more preferably in a concentration of greater than 5 $mol.l^{-1}$

The conditions of temperature and pressure are preferably selected to yield a product slate with a K-factor within the range of from 0.40 to 0.90, preferably in the range of from 0.45 to 0.90. In the present invention, polymerisation is deemed to have occurred when a product slate has a K-factor greater than 0.9.

The co-oligomerisation reaction can be carried out in the gas phase or liquid phase, or mixed gas-liquid phase, depending upon the volatility of the feed and product olefins.

The co-oligomerisation reaction may be carried out in the presence of an inert solvent which may also be the carrier for the catalyst and/or feed olefins. Suitable solvents include alkanes, alkenes, cycloalkanes, and aromatic hydrocarbons.

For example, solvents that may be suitably used include hexane, isooctane, benzene, toluene, and xylene.

Reaction times of from 0.1 to 10 hours have been found to be suitable, dependent on the activity of the catalyst. The reaction is preferably carried out in the absence of air or moisture.

The co-oligomerisation reaction may be carried out in a conventional fashion. It may be carried out in a stirred tank reactor, wherein olefins and catalysts or catalyst precursors are added continuously to a stirred tank and reactants, products, catalysts, and unused reactants are removed from the stirred tank with the products separated and the catalysts and unused reactants recycled back to the stirred tank.

Alternatively, the reaction may be carried out in a batch reactor, wherein the catalyst precursors, and reactant olefins are charged to an autoclave, and after being reacted for an appropriate time, products are separated from the reaction mixture by conventional means, such as distillation.

After a suitable reaction time, the co-oligomerisation reaction can be terminated by rapid venting of the ethylene in order to deactivate the catalyst system.

The resulting product composition may comprise linear alpha olefins and/or alkyl-branched alpha olefins.

In a preferred embodiment, the product composition may comprise linear alpha olefins and/or methyl-branched alpha olefins and/or ethyl-branched alpha olefins, that is to say wherein R_{16} is methyl or ethyl.

The product composition of the present invention will generally comprise greater than 5 % wt, preferably greater than 10 % wt, more preferably greater than 15 % wt, and most preferably greater than 25 % wt alkyl-branched alpha olefins based on the total weight of linear alpha olefins and alkyl-branched alpha olefins in the product composition.

Said linear alpha olefins and/or alkyl-branched alpha olefins may have a chain length of from 4 to 100 carbon atoms, preferably 4 to 30 carbon atoms, and most preferably from 4 to 20 carbon atoms.

Product olefins can be recovered suitably by distillation and further separated as desired by distillation techniques dependent on the intended end use of the olefins.

The present invention will now be illustrated by the following Examples, which should not be regarded as limiting the scope of the present invention in any way, by reference to the accompanying drawings, in which:-

Figure 1 is a regression analysis of Example 4;

Figure 2 is a GC-trace of product of Example 5; and

Figure 3 is a partial gas chromatography (GC) trace of product from Example 9.

General Procedures and Characterisation

All the operations with the catalyst systems were carried out under nitrogen atmosphere. All solvents used were dried using standard procedures.

Anhydrous toluene (99.8% purity) (ex. Aldrich) was dried over 4Å molecular sieves (final water content of about 3 ppm).

Ethylene (99.5% purity) was purified over a column containing 4Å molecular sieves and BTS catalyst (ex. BASF) in order to reduce water and oxygen content to <1 ppm.

1-Octene (99.8% 1-octene content; the remainder being 0.1% 1-hexene and 0.1% 1-decene) and 1-hexadecene (94.1% 1-hexadecene content; the remainder being 3.6% 1-tetradecene and 2.3% 1-octadecene) were SHOP alpha olefins obtained from Shell Chemicals and were purified by treatment with basic alumina and subsequent drying over 4Å molecular sieves in a nitrogen atmosphere. 1-Heptene (99.3% 1-heptene content; the remainder being heptene isomers) was obtained from Aldrich and was used after drying over 4Å molecular sieves in a nitrogen atmosphere.

1-Aminonaphthalene, 2,6-Diacetylpyridine, 3,5-dimethylaniline, 2,5-dimethylaniline, 2,4,6-trimethylaniline, 2-*tert*-butylaniline, 4-*tert*-butylaniline, 2,6-difluoroaniline, 2-fluoroaniline and anhydrous iron (II) chloride are available ex. Aldrich. 1-Aminopyrrole was purchased from TCI, Japan.

Ferrocenylamine was prepared according to the method outlined in the literature (D. van Leusen and B. Hessen, Organometallics, **2001**, *20*, 224-226).

The oligomers obtained were characterised by Gas Chromatography (GC), in order to evaluate oligomer distribution, using a HP 5890 series II apparatus and the following chromatographic conditions:

Column: HP-1 (cross-linked methyl siloxane), film thickness = 0.25μm, internal diameter = 0.25 mm, length 60 m (by Hewlett Packard); injection temperature: 325°C;

detection temperature: 325°C; initial temperature: 40°C for 10 minutes; temperature programme rate: 10.0°C/minute; final temperature: 325°C for 41.5 minutes; internal standard: n-hexylbenzene. Response factors for the even linear alpha olefins relative to n-hexylbenzene (internal standard) were determined using a standard calibration mixture. Response factors for the even-numbered branched alpha olefins, the odd-numbered linear and branched alpha olefins were assumed to be equal to the even linear alpha olefins of the same or similar carbon number. The yields of the C_4-C_{30} olefins were obtained from the GC analysis, from which the K(linear)-factors were determined by regression analysis, generally using the C_{10}-C_{28} data of the linear alpha olefins. In the ethene/1-octene co-oligomerisation the 1-octene content was calculated from the regression analysis of the linear alpha olefins in the C_{10}-C_{28} range. In the ethene/1-hexadecene co-oligomerisation the 1-hexadecene content was calculated from the regression analysis of the linear alpha olefins in the C_{18}-C_{28} range.

The relative amounts of the linear (lin.) 1-hexene amongst all hexene isomers and the relative amount of linear (lin.) 1-dodecene amongst all dodecene isomers found from the GC analysis is used as a measure of the selectivity of the catalyst towards linear alpha-olefin formation.

The yields of the branched C_{10}-C_{30} alpha olefins in case of ethene/1-octene co-oligomerisation, or the branched C_{18}-C_{30} alpha olefins in case of ethene/1-hexadecene co-oligomerisation, were obtained from the GC analysis, from which the K(branched)-factors were determined by regression analysis. In the case of co-

oligomerisation of ethene and 1-heptene the yields of the odd linear and branched C_9-C_{29} alpha olefins were obtained from the GC analysis, from which their K(linear)-factor and their K(branched)-factor were determined by regression analysis.

The weight ratio of alkyl-branched 1-undecene(s) over alkyl-branched and linear 1-undecenes, the weight ratio of alkyl-branched 1-dodecene(s) over alkyl-branched and linear 1-dodecenes and the weight ratio of alkyl-branched 1-eicocene(s) over alkyl-branched and linear 1-eicocenes determined by GC analysis are used as a measure of the selectivity of the catalyst towards the formation of alkyl-branched alpha-olefins.

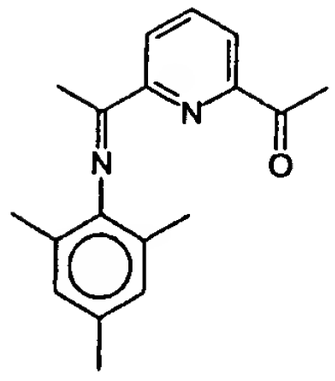
The NMR data were obtained at room temperature with a Varian 300 or 400 MHz apparatus. Structural assignments of linear alpha-olefins and by-products were made by comparison of ^{1}H- and ^{13}C-NMR spectra of reaction samples containing different amounts of various components. Characteristic resonances for olefinic and linear and branched aliphatic groups were taken from literature. Where deemed necessary, techniques allowing identification of carbon-carbon connectivities were applied to provide additional structural proof.

Catalyst Components

1. Preparation of 2,6-bis-[1-(2-methylphenylimino) ethyl]pyridine iron[II] chloride complex (X)

Complex X was prepared according to the method disclosed in WO-A-99/02472.

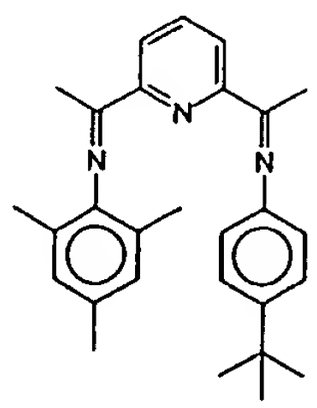
2. Preparation of 2-[1-(2,4,6-trimethylphenylimino) ethyl]-6-acetylpyridine (1)



(1)

2,6-Diacetylpyridine (7.3 g, 44.8 mmol) and 2,4,6-trimethylaniline (5.74 g, 42.55 mmol) were dissolved in 450 ml of toluene. To this solution, 4Å molecular sieves and a small amount of *p*-toluenesulphonic acid (0.22 mmol) were added. The mixture was refluxed for 16 hours. After filtration the solvent was removed in vacuo. Several crystallisations from ethanol yielded 3.42 g (28.7%) of monoimine (1). ^{1}H-NMR ($CDCl_3$) δ 8.55 (d, 1H, Py-H_m), 8.11(d, 1H, Py-H_m), 7.92 (t, 1H, Py-H_p), 6.89 (s, 2H, ArH), 2.77(s, 3H, Me), 2.27 (s, 3H, Me), 2.22 (s, 3H, Me), 1.99 (s, 6H, Me).

3. Preparation of 2-[1-(2,4,6-trimethylphenylimino) ethyl]-6-[1-(4-*tert*-butylphenylimino)ethyl]pyridine (2)

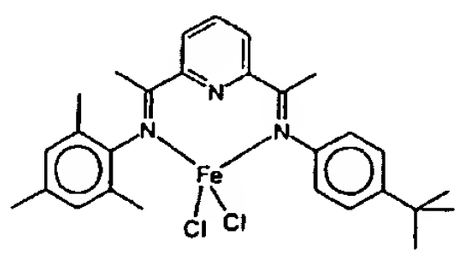


(2)

Monoimine (1, 2.8 g, 10 mmol) and 4-*tert*-butylaniline (1.49 g, 10 mmol) were dissolved in 100 ml of toluene. To this solution, 4Å molecular sieves and a small amount of *p*-toluenesulphonic acid (0.1 mmol) were added. After

standing for 5 days with addition of more 4Å molecular sieves, the mixture was refluxed for 2 hours. After filtration the solvent was removed in vacuo. The residue was washed with methanol and recrystallised from ethanol. Yield 2.4 g (58%) of mixed diimine (2). ^{1}H-NMR ($CDCl_3$) δ 8.42 (d, 1H, Py-H_m), 8.34 (d, 1H, Py-H_m), 7.86 (t, 1H, Py-H_p), 7.38 (d, 2H, ArH), 6.89 (s, 2H, ArH), 6.78 (d, 2H, ArH), 2.42 (s, 3H, Me), 2.29 (s,3H, Me), 2.22 (s, 3H, Me), 2.00 (s, 6H, Me), 1.34 (s, 9H, Bu^t).

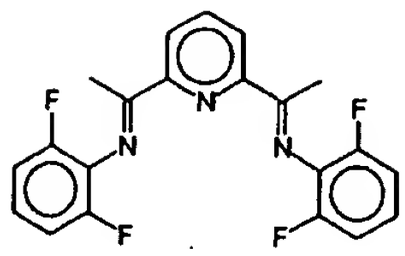
4. Preparation of 2-[1-(2,4,6-trimethylphenylimino) ethyl]-6-[1-(4-*tert*-butylphenylimino) ethyl] pyridine iron[II] chloride complex (3)



(3)

In an inert atmosphere a solution of 1.5 g diimine (2, 3.6 mmol) in 100 ml dichloromethane was added to 420 mg $FeCl_2$ (3.3 mmol) in 150 ml dichloromethane. The mixture was stirred for one week. The developed blue precipitate was isolated by filtration and dried in vacuo. Yield 1.5 g (84%) of iron complex (3). ^{1}H-NMR ($Cl_2CDCDCl_2$, broad signals) d 79.3 (1H, Py-H_m), 77.7 (1H, Py-H_m), 27.0 (1H, Py-H_p), 20.7 (3H, Me), 17.3 (6H, Me), 15.0 (2H, ArH), 14.3 (2H, ArH), 1.2 (9H, Bu^t), -2.6 (3H, MeC=N), -17.9 (2H, *o*-ArH), -32.1 (3H, MeC=N).

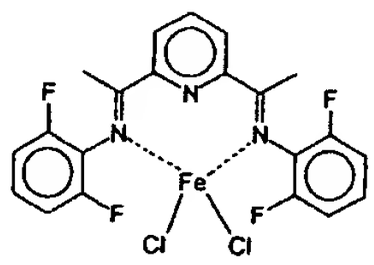
5. Preparation of 2,6-bis-[1-(2,6-difluorophenylimino) ethyl] pyridine (4)



(4)

2,6-Diacetylpyridine (1.76 g, 10.8 mmol) and 2,6-difluoroaniline (2.94 g, 22.8 mmol) were dissolved in 50 ml of toluene. To this solution, 4Å molecular sieves were added. After standing for 3 days, with addition of more 4Å molecular sieves the mixture was filtered. The solvent was removed in vacuo. The residue was crystallised from ethanol. Yield of 4: 1 g (24%). ^{1}H-NMR ($CDCl_3$) δ 8.44 (d, 2H, Py-H_m), 7.90 (t, 1H, Py-H_p), 7.05 (m, 2H, ArH) 6.96 (m, 4H, ArH), 2.44 (s, 6H, Me). ^{19}F-NMR ($CDCl_3$) δ -123.6.

6. 2,6-bis-[1-(2,6-difluorophenylimino)ethyl] pyridine iron[II] chloride complex (5)



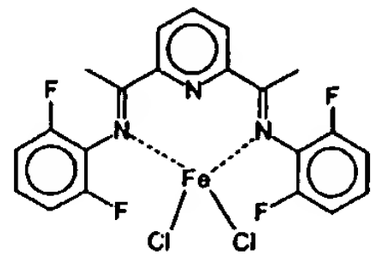
(5)

In an inert atmosphere 493 mg diimine (4, 1.27 mmol) was dissolved in 50 ml THF. $FeCl_2$ (162 mg , 1.28 mmol) in 10 ml THF was added. After stirring for 16 hours at room temperature, the solvent was removed in vacuo. Toluene (100 ml) was added. The blue precipitate was isolated by filtration, washed with pentane and dried in vacuo.

Isolated 0.5 g (76%) of iron complex 5. ^{1}H-NMR ($Cl_2CDCDCl_2$, broad signals) δ 75.5 (2H, Py-H_m), 39.6

(1H, Py-H_p), 15.7 (4H, ArH), -11.6 (2H, ArH), -22.4 (6H, MeC=N). ^{19}F-NMR ($Cl_2CDCDCl_2$) δ -70.3.

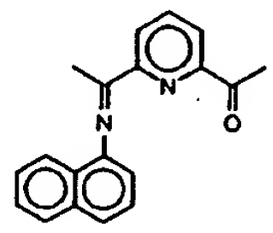
7. Alternate preparation of 2,6-bis-[1-(2,6-difluorophenylimino)ethyl] pyridine iron[II] chloride complex (5')



(5')

In an inert atmosphere a solution of 60 mg $FeCl_2$ (0.47 mmol) in 0.5 ml ethanol was slowly added to a solution of 260 mg diimine (4, 0.67 mmol) in a solvent mixture of 10 ml toluene and 6 ml pentane. The resulting blue precipitate was isolated by centrifugation, washed three times with toluene and dried in vacuo. Yield 210 mg (87%) of iron complex 5'. ^{1}H-NMR (CD_2Cl_2, broad signals) δ 76.7 (2H, Py-H_m), 37.6 (1H, Py-H_p), 16.8 (4H, ArH), -10.2 (2H, ArH), -20.3 (6H, MeC=N). ^{19}F-NMR (CD_2Cl_2) δ -75.

8. Preparation of 2-[1-(1-naphthylimino)ethyl]-6-acetylpyridine (6)

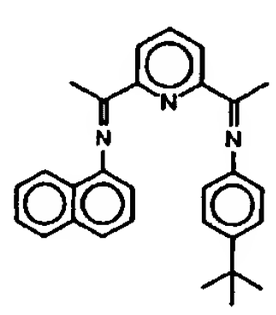


(6)

2,6-Diacetylpyridine (5.49 g, 33.6 mmol) and 1-aminonaphthalene (4.8 g, 33.5 mmol) were dissolved in 100

ml of toluene. To this solution molecular sieves (4Å) were added. After standing for 20 hours at room temperature, the mixture was filtered. The solvent was removed in vacuo. The resulting mixture of 2,6-diacetylpyridine, 2,6-bis-[1-(1-naphthylimino)ethyl] pyridine and 2-[1-(1-naphthylimino)ethyl]-6-acetylpyridine was dissolved in 50 ml THF. The diiminepyridine by-product 2,6-bis-[1-(1-naphthylimino)ethyl]pyridine was removed by selective complexation to a metal halide. $FeCl_2$ (0.79 g , 6.23 mmol) was added in an inert atmosphere. After stirring for 16 hours at room temperature, the solvent was removed in vacuo. Toluene (100 ml) was added to the resulting mixture. The precipitated complex was filtered off over a small layer of silica, yielding a yellow solution. The solvent was removed vacuo. Crystallisation from ethanol yielded 3.25g of 2-[1-(1-naphthylimino)ethyl]-6-acetylpyridine (6) (33.6%). ^{1}H-NMR ($CDCl_3$) δ 8.65 (d, 1H, Py-H_m), 8.15 (d, 1H, Py-H_m), 7.95 (t, 1H, Py-H_p), 7.87 (d, 1H, ArH), 7.76 (d, 1H, ArH), 7.64 (d, 1H, ArH), 7.4-7.6 (m, 3H, ArH), 6.82 (d, 1H, ArH), 2.79 (s, 3H, Me), 2.38 (s, 3H, Me).

9. Preparation of 2-[1-(1-naphthylimino)ethyl]-6-[1-(4-*tert*-butylphenylimino)ethyl] pyridine (7)

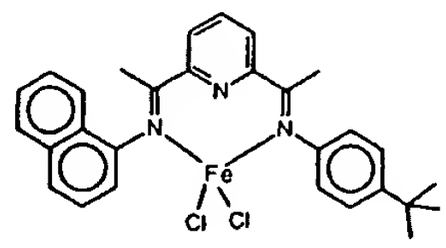


(7)

Monoimine (6, 1.25 g, 4.34 mmol) and 4-*tert*-butylaniline (0.65 g, 4.34 mmol) were dissolved in 50 ml of toluene.

To this solution, molecular sieves (4Å) were added. After standing for 16 hours the mixture was filtered. The solvent was removed in vacuo. The residue was recrystallised from ethanol. Yield 0.44 g (24%) of mixed diimine (7, 96% purity by NMR). ^{1}H-NMR ($CDCl_3$) δ 8.51 (d, 1H, Py-H_m), 8.38 (d, 1H, Py-H_m), 7.91 (t, 1H, Py-H_p), 7.86 (d, 1H, ArH), 7.78 (d, 1H, ArH), 7.63 (d, 1H, ArH), 7.4-7.6 (m, 5H, ArH), 6.8-6.9 (m, 3H, ArH), 2.43 (s, 3H, Me), 2.37 (s, 3H, Me), 1.34 (s, 9H, Bu^t).

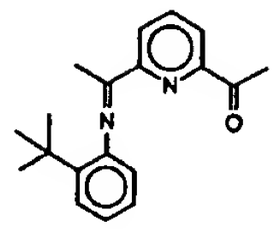
10. Preparation of 2-[1-(1-naphthylimino)ethyl]-6-[1-(4-*tert*-butylphenylimino)ethyl] pyridine iron[II] chloride complex (8)



(8)

In an inert atmosphere, a solution of 440 mg diimine (7, 1.05 mmol) in 5 ml dichloromethane was added to 130 mg $FeCl_2$ (1.03 mmol) in 20 ml dichloromethane. The mixture was stirred for 9 days. Addition of 10 ml pentane yielded a blue precipitate, which was isolated by centrifugation and dried in vacuo. Yield 480 mg (85%) of iron complex (8) ^{1}H-NMR ($Cl_2CDCDCl_2$), gave broad signals which were not further assigned.

11. Preparation of 2-[1-(2-tert-butylphenylimino)ethyl]-6-acetylpyridine (9)



(9)

2,6-Diacetylpyridine (4.37 g, 26.78 mmol) and 2-*tert*-butylaniline (4.0 g, 26.8 mmol) were dissolved in 100 ml of toluene. To this solution, molecular sieves (4Å) were added. After standing for 20 hours at room temperature, the mixture was filtered. The solvent was removed in vacuo.

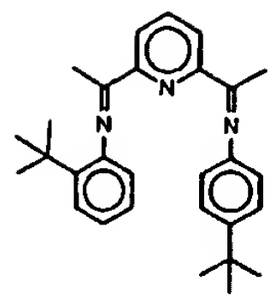
The resulting mixture of 2,6-diacetylpyridine, 2,6-bis-[1-(2-*tert*-butylphenylimino)ethyl]pyridine and 2-[1-(2-*tert*-butylphenylimino)ethyl]-6-acetylpyridine was dissolved in 50 ml THF. The diiminepyridine by-product 2,6-bis-[1-(2-*tert*-butylphenylimino)ethyl]pyridine was removed by selective complexation to a metal halide.

$FeCl_2$ (0.79 g , 6.23 mmol) was added in an inert atmosphere. After stirring for 16 hours at room temperature, the solvent was removed in vacuo.

Toluene (100 ml) was added to the resulting mixture. The precipitated complex was filtered off over a small layer of silica, yielding a yellow solution. The solvent was removed in vacuo.

Crystallisation from ethanol yielded 2.8 g of 2-[1-(2-*tert*-butylphenylimino)ethyl]-6-acetylpyridine (9) (36%). ^{1}H-NMR ($CDCl_3$) δ 8.48 (d, 1H, Py-H_m), 8.10 (d, 1H, Py-H_m), 7.93 (t, 1H, Py-H_p), 7.41 (d, 1H, ArH), 7.17 (t, 1H, ArH), 7.07 (t, 1H, ArH), 6.51 (d, 1H, ArH), 2.77 (s, 3H, Me), 2.38 (s, 3H, Me), 1.33 (s, 9H, Bu^t).

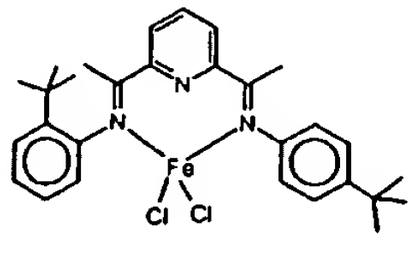
12. Preparation of 2-[1-(2-tert-butylphenylimino)ethyl]-6-[1-(4-tert-butylphenylimino)ethyl] pyridine (10)



(10)

Monoimine (9,1.06 g, 3.6 mmol) and 4-*tert*-butylaniline (0.56 g, 3.75 mmol) were dissolved in 25 ml of toluene. To this solution, molecular sieves (4Å) were added. After standing for 60 hours the mixture was filtered. The solvent was removed in vacuo. The residue was recrystallised from ethanol. Yield 0.81 g (53 %) of mixed diimine (10). ^{1}H-NMR ($CDCl_3$) δ 8.36 (d, 1H, Py-H_m), 8.34 (d, 1H, Py-H_m), 7.88 (t, 1H, Py-H_p), 7.4 (m, 3H, ArH), 7.18 (t, 1H, ArH), 7.07 (t, 1H, ArH), 6.78 (d, 2H, ArH), 6.54 (d, 1H, ArH), 2.42 (s, 3H, Me), 2.38 (s, 3H, Me), 1.35 (s, 9H, Bu^t), 1.34 (s, 9H, Bu^t).

13. Preparation of 2-[1-(2-*tert*-butylphenylimino)ethyl]-6-[1-(4-*tert*-butylphenylimino)ethyl] pyridine iron[II] chloride complex (11)

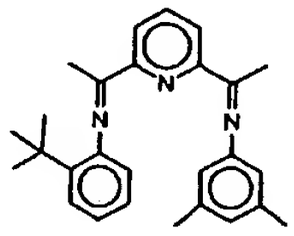


(11)

In an inert atmosphere, a solution of 640 mg diimine (10, 1.5 mmol) in 10 ml dichloromethane was added to 182 mg $FeCl_2$ (1.44 mmol) in 20 ml dichloromethane. The mixture was stirred for 16 hrs. Addition of 20 ml pentane yielded a blue precipitate. Isolation and drying in vacuo yielded 650 mg (82%) of iron complex (11). ^{1}H-NMR (CD_2Cl_2, broad

signals) δ 81.9 (1H, Py-H_m), 77.5 (1H, Py-H_m), 30.4 (1H, Py-H_p), 16.4 (1H, ArH), 13.8 (2H, ArH), 6.3 (1H, ArH), 1.5 (9H, Bu^t), 1.1 (9H, Bu^t), -1.0 (3H, MeC=N), -12.7 (1H, ArH), -21.3 (2H, *o*-ArH), -33.1 (3H, MeC=N), -33.7 (1H, *o*-ArH).

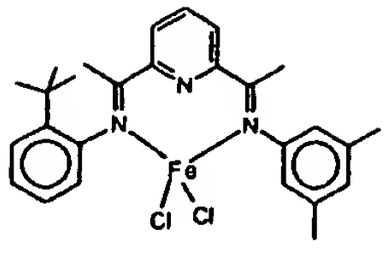
14. Preparation of 2-[1-(2-*tert*-butylphenylimino)ethyl]-6-[1-(3,5-dimethylphenylimino)ethyl] pyridine (12)



(12)

Monoimine (9,1.13 g, 3.87 mmol) and 3,5-dimethylaniline (0.5 g, 4.13 mmol) were dissolved in 25 ml of toluene. To this solution, molecular sieves (4Å) were added. After standing for 60 hours the mixture was filtered. The solvent was removed in vacuo. The residue was recrystallised from ethanol. Yield 0.79 g (52 %) of mixed diimine (12). ^{1}H-NMR ($CDCl_3$) δ 8.37 (d, 1H, Py-H_m), 8.32 (d, 1H, Py-H_m), 7.87 (t, 1H, Py-H_p), 7.42 (d, 1H, ArH), 7.18 (t, 1H, ArH), 7.07 (t, 1H, ArH), 6.76 (s, 1H, ArH), 6.54 (d, 1H, ArH), 6.46 (s, 2H, ArH), 2.40 (s, 3H, Me), 2.39 (s, 3H, Me), 2.33 (s, 3H, Me), 1.36 (s, 9H, Bu^t).

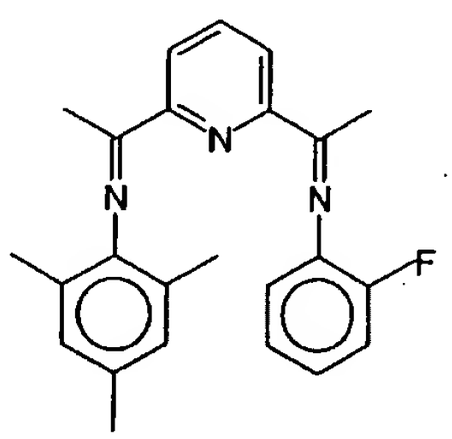
15. Preparation of 2-[1-(2-*tert*-butylphenylimino)ethyl]-6-[1-(3,5-dimethylphenylimino)ethyl] pyridine iron[II] chloride complex (13)



(13)

In an inert atmosphere, a solution of 617 mg diimine (12, 1.55 mmol) in 10 ml dichloromethane was added to 187 mg $FeCl_2$ (1.48 mmol) in 20 ml dichloromethane. The mixture was stirred for 16 hours. Addition of 20 ml pentane yielded a blue precipitate. Cooling to -30 °C yielded a second amount of blue precipitate. Isolation and drying in vacuo yielded 660 mg (85%) of iron complex (13) ^{1}H-NMR (CD_2Cl_2, broad signals) δ 81.5 (1H, Py-H_m), 76.9 (1H, Py-H_m), 37.6(1H, Py-H_p), 16.1 (1H, ArH), 1.2 (1H, ArH), 1.0 (9H, Bu^t), -2.7 (3H, MeC=N), -5.6 (6H, Me), -11.7 (1H, ArH), -13.5 (1H, ArH), -25.6 (2H, *o*-ArH), -35.7 (3H, MeC=N), -37.4 (1H, *o*-ArH).

16. Preparation of 2-[1-(2,4,6-trimethylphenylimino) ethyl]-6-[1-(2-fluorophenylimino)ethyl]pyridine (14)



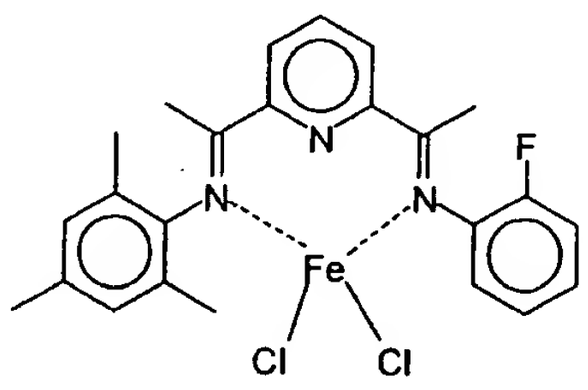
(14)

Monoimine (1, 1.0 g, 3.57 mmol) and 2-fluoroaniline (398 mg, 3.57 mmol) were dissolved in 50 ml of toluene. To this solution, 4Å molecular sieves were added. After standing for 20 hours, with addition of more molecular

sieves, the mixture was filtered. The solvent was removed in vacuum and the oily residue was warmed in ethanol (50°C). The yellow solid, which precipitated after cooling at -20°C, was filtered off and dried in vacuo. Yield 300 mg (23 %) of mixed diimine (14).

^{1}H-NMR ($CDCl_3$) δ 8.45 (d, 1H, Py-H_m), 8.38 (d, 1H, Py-H_m), 7.88 (t, 1H, Py-H_p), 7.1 (m, 4H, ArH), 6.93 (dd, 2H, ArH), 6.89 (s, 2H, ArH), 2.41 (s, 3H, Me), 2.29 (s, 3H, Me), 2.22 (s, 3H, Me), 2.00 (s, 6H, Me). ^{19}F-NMR ($CDCl_3$) δ -126.8.

17. Preparation of 2-[1-(2,4,6-trimethylphenylimino) ethyl]-6-[1-(2-fluorophenylimino)ethyl]pyridine iron[II] chloride complex (15)



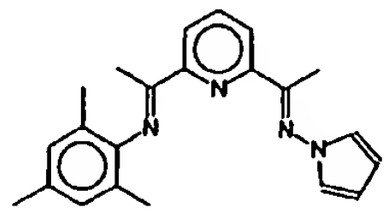
(15)

In an inert atmosphere, a solution of 270 mg diimine (14, 0.72 mmol) in 5 ml dichloromethane was added to 87 mg $FeCl_2$ (0.67 mmol) in 20 ml dichloromethane. The mixture was stirred for 20 hours. Addition of 10 ml pentane yielded a blue precipitate, which was isolated by centrifugation and dried in vacuo. Yield 175 mg (51%) of iron complex (15).

^{1}H-NMR (CD_2Cl_2 , broad signals, selective data) δ 84.5 (1H, Py-H_m), 80.4 (1H, Py-H_m), 21.2 (1H, Py-H_p), 4.5

(3H, MeC=N), -24.5 (1H, o-ArH), -38.1 (3H, MeC=N). ^{19}F-NMR (CD_2Cl_2) δ -95.0.

18. Preparation of 2-[1-(2,4,6-trimethylphenylimino) ethyl]-6-[1-(1-pyrrolylimino)ethyl]pyridine (16)

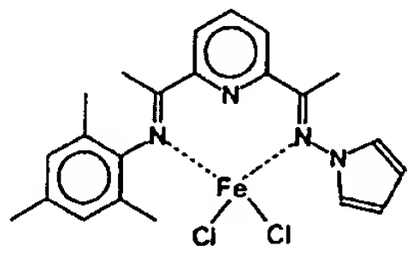


(16)

Monoimine ((1), 3.0 g, 10.7 mmol) and 1-aminopyrrole (1.0 g, 12.18 mmol) were dissolved in 50 ml of toluene. To this solution, molecular sieves (4Å) were added. After standing for 40 hours the mixture was filtered. The solvent was removed in vacuo. The residue was recrystallised from ethanol. Yield 1.85 g (50 %) of mixed diimine (16).

^1H-NMR ($CDCl_3$) δ 8.42 (d, 1H, Py-H_m), 8.29 (d, 1H, Py-H_m), 7.86 (t, 1H, Py-H_p), 6.93 (m, 2H, Pyrrole-H), 6.88 (s, 2H, ArH), 6.26 (m, 2H, Pyrrole-H), 2.67 (s, 3H, Me), 2.28 (s, 3H, Me), 2.20 (s, 3H, Me), 2.00 (s, 6H, Me).

19. Preparation of 2-[1-(2,4,6-trimethylphenylimino) ethyl]-6-[1-(1-pyrrolylimino)ethyl]pyridine iron[II] chloride complex (17)



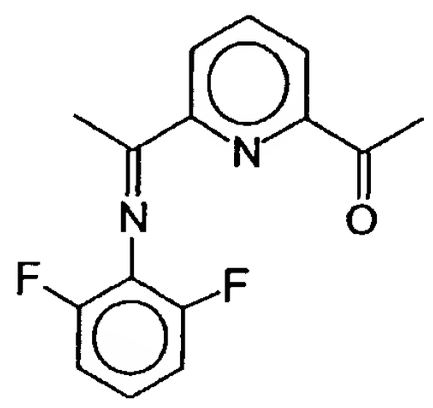
(17)

In an inert atmosphere, a solution of 103 mg $FeCl_2$ (0.81 mmol) in 0.7 ml ethanol was slowly added to a

solution of 400 mg diimine ((16), 1.16 mmol) in a solvent mixture of 10 ml toluene and 6 ml pentane. The green-brown precipitate was isolated by centrifugation, washed three times with toluene and dried in vacuo. Yield 375 mg (98%) of iron complex (17).

^{1}H-NMR (CD_2Cl_2, broad signals, not assigned) δ 88.1 (1H), 72.4 (1H), 29.9 (3H), 19.5 (3H), 16.9 (6H), 13.5 (2H), 8.8 (2H), 5.8 (2H), 2.9 (1H), -45.1 (3H).

20. Preparation of 2-[1-(2,6-difluorophenylimino)ethyl]-6-acetylpyridine (18)



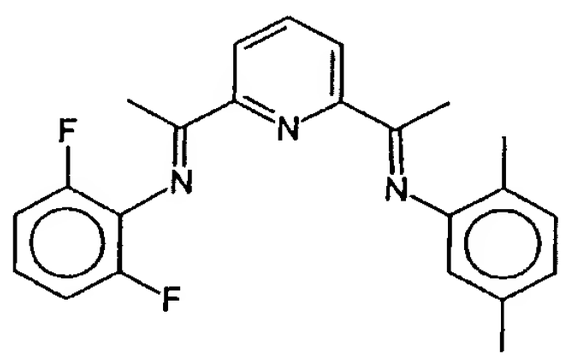
(18)

2,6-Diacetylpyridine (4.04 g, 24.7 mmol) and 2,6-difluoroaniline (3.2 g, 24.7 mmol) were dissolved in 50 ml of toluene. To this solution, molecular sieves (4Å) were added. After standing for 5 days at room temperature, the mixture was filtered. The solvent was removed in vacuo. From the resulting mixture of 2,6-diacetylpyridine, monoimine, and diimine. Most of the 2,6-diacetylpyridine was removed by sublimation in vacuo at 80-90 °C. The residue contained based on ^{1}H-NMR data 0.35 mmol 2,6-diacetylpyridine , 1.28 mmol diimine and 5.46 mmol monoimine. This mixture was reacted with 162 mg (1.28 mmol) $FeCl_2$ in 10 ml THF to remove the diimine. After stirring for 16 h at room temperature, the solvent was removed in vacuo. Toluene (50 ml) was added to the

resulting mixture. The precipitated complex was filtered off over a small layer of silica, yielding a yellow solution. The solvent was removed in vacuo. Crystallisation from ethanol yielded 1.35 g of 2-[1-(2,6-difluorophenylimino)ethyl]-6-acetylpyridine (18) (19.8 %).

^{1}H-NMR ($CDCl_3$): δ 8.52 (d, 1H, Py-H_m), 8.12 (d, 1H, Py-H_m), 7.92 (t, 1H, Py-H_p), 7.03 (m,1H, ArH), 6.97 (m, 2H, ArH), 2.77 (s, 3H, Me), 2.43 (s, 3H, Me). ^{19}F-NMR ($CDCl_3$): δ -123.6.

21. Preparation of 2-[1-(2,6-difluorophenylimino)ethyl]-6-[1-(2,5-dimethylphenylimino)ethyl]pyridine (19)



(19)

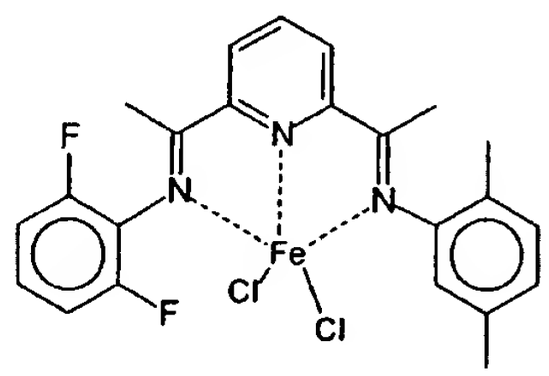
Monoimine (18, 0.86 g, 3.13 mmol) and 2,5-dimethylaniline (0.40 g, 3.3 mmol) were dissolved in 25 ml of toluene. To this solution, molecular sieves (4Å) were added. After standing for 3 days the mixture was filtered. The solvent was removed in vacuo. The residue was crystallised from ethanol. A mixture of 2-[1-(2,6-difluorophenylimino)ethyl]-6-[1-(2,5-dimethylphenylimino)ethyl]pyridine and 2,6-bis{2-[1-(2,5-dimethylphenylimino)ethyl]}pyridine was isolated. In THF 2,6-bis{2-[1-(2,5-dimethylphenylimino)ethyl]}pyridine was co-ordinated to $FeCl_2$. The solvent was removed in vacuo. Toluene (10 ml) was added to the resulting mixture. The precipitated complex was filtered off over a small layer

of silica, yielding a yellow solution. The solvent was removed in vacuo. Crystallisation from ethanol yielded 40 mg (3%) of 2-[1-(2,6-difluorophenylimino)ethyl]-6-[1-(2,5-dimethylphenylimino)ethyl]pyridine (19).

^{1}H-NMR ($CDCl_3$) δ 8.41 (d, 2H, Py-H_m), 7.89 (t, 1H, Py-H_p), 6.8-7.2 (m, 5H, ArH), 6.50 (s, 1H, ArH), 2.44 (s, 3H, Me), 2.32 (s, 6H, Me), 2.05(s, 3H, Me).

^{19}F-NMR ($CDCl_3$): δ -123.4

22. Preparation of 2-[1-(2,6-difluorophenylimino)ethyl]-6-[1-(2,5-dimethylphenylimino)ethyl]pyridine iron[II] chloride complex (20)

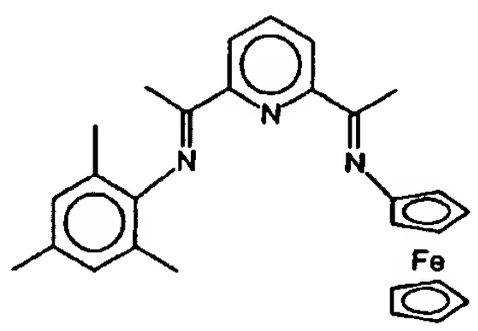


(20)

In an inert atmosphere a solution of 35 mg diimine (19, 0.093 mmol) in 5 ml dichloromethane was added to 11 mg $FeCl_2$ (0.086 mmol) in 10 ml dichloromethane. The mixture was stirred for 16 hours. After addition of 5 ml pentane the resulting blue precipitate was isolated by centrifugation, washed with pentane and dried in vacuo. Yield 40 mg (90%) of iron complex 20.

^{1}H-NMR ($Cl_2CDCDCl_2$, broad signals) δ 78.6 (1H, Py-H_m), 75.0 (1H, Py-H_m), 37.9 (1H, Py-H_p), 19.8 (1H, ArH), 16.6 (3H, Me) 15.8 (1H, ArH), 15.6 (1H, ArH), -8.2 (3H, Me) -9.7 (1H, ArH), -10.8 (3H, MeC=N), -15.7 (1H, ArH), -22.4 (1H, ArH), -29.8 (3H, MeC=N). ^{19}F-NMR ($Cl_2CDCDCl_2$) δ -62.7 and -67.4.

23. Preparation of 2-[1-(2,4,6-trimethylphenylimino) ethyl]-6-[1-(ferrocenylimino)ethyl]pyridine (21)

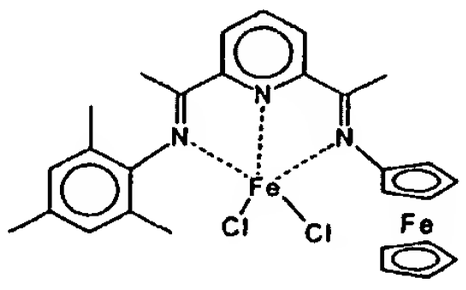


(21)

Monoimine 2-[1-(2,4,6-trimethylphenylimino)ethyl]-6-acetylpyridine (1, 263 mg, 0.94 mmol) and ferrocenylamine (280 mg, 1.03 mmol) were dissolved in 40 ml of toluene. To this solution, molecular sieves (4Å) were added. After standing for 16 hours the mixture was filtered. The solvent was removed in vacuo. The residue was recrystallised from ethanol. Yield 180 mg (41 %) of mixed diimine 21.

^{1}H-NMR (CD_2Cl_2) δ 8.36 (dd, 2H, Py-H_m), 7.85 (t, 1H, Py-H_p), 6.88 (s, 2H, ArH), 4.46 (t, 2H, CpH), 4.25 (t, 2H, CpH), 4.20 (s, 5H, CpH), 2.55 (s, 3H, Me), 2.27 (s, 3H, Me), 2.20 (s, 3H, Me), 1.98 (s, 6H, Me).

24. Preparation of 2-[1-(2,4,6-trimethylphenylimino) ethyl]-6-[1-(ferrocenylimino)ethyl]pyridine iron[II] chloride complex (22)



(22)

In an inert atmosphere a solution of 153 mg diimine (21, 0.33 mmol) in 5 ml dichloromethane was added to 41 mg $FeCl_2$ (0.32 mmol) in 5 ml dichloromethane. The mixture was stirred for 16 h. The blue-gray precipitate was isolated by centrifugation, washed with hexane and dried in vacuo. Yield 170 mg (89 %) of iron complex 22.

^{1}H-NMR (CD_2Cl_2, broad signals, selected data) δ 88.6 (1H, Py-H_m), 76.7 (1H, Py-H_m), 21.3 (3H, Me), 16.3 (6H, Me), 2.8 (5H, CpH), -11.5 (3H, MeC=N).

25. Methylaluminoxane (MAO)

The MAO-solution in toluene (Eurecen AL 5100/10T, batch: B7683; [Al] = 4.88%wt, TMA = 35.7 wt% (calculated), Molecular mass = 900 g/mol) used was ex. Witco GmbH, Bergkamen, Germany.

Catalyst system preparation

Catalyst preparation was carried out under nitrogen in a Braun MB 200-G dry box.

The iron complex (typically about 10 mg) was placed in a glass bottle sealed by a septum; the MAO-solution (4.0 g), of the above mentioned grade, was added and stirred for 2 minutes. This yielded generally a dark-coloured solution, which sometimes contained some precipitate. Thereafter toluene (9.0 g) was added and the solution was stirred for another 10 min. Immediately hereafter, part of this solution was used in the oligomerisation reaction (see Table 1 for the amounts used).

Oligomerisation Experiments

Oligomerisation experiments were carried out in a 1-litre steel autoclave equipped with jacket cooling with a heating/cooling bath (ex. Julabo, model no. ATS-2) and a turbine/gas stirrer and baffles. In order to remove

traces of water from the reactor, it was evacuated overnight at <10 Pa, at 70°C. The reactor was scavenged by introducing 250 ml toluene and MAO (0.3-1.2 g solution) and subsequent stirring at 70°C under nitrogen pressure of 0.4-0.5 MPa for 30 min. The reactor contents were discharged via a tap in the base of the autoclave. The reactor was evacuated to 0.4 kPa and loaded with about 250 ml toluene, 1-heptene, 1-octene or 1-hexadecene (the precise amounts are mentioned in Table 1) and heated to 40 °C and pressurised with ethylene to the pressure indicated in Table 1 or in the description of the experiment. The MAO-solution (typically 0.5 g) was then added to the reactor with the aid of toluene (the total volume injected was 30 ml, using a procedure similar to the injection of the catalyst; see below) and the stirring at 800 rpm was continued for 30 minutes. The catalyst system prepared as described above and in an amount as described in Table 1, was introduced into the stirred reactor using an injection system with the aid of toluene (the total volume injected was 30 ml: the catalyst solution diluted with toluene to 10 ml was injected and the injector system was rinsed twice with 10 ml toluene). Addition of the catalyst solution resulted in an exotherm (generally 5-20 °C), which reached a maximum within 1 minute and was followed by rapid establishment of the temperature and pressure indicated in Table 1. Temperature and pressure were monitored throughout the reaction, as well as ethylene consumption, whilst maintaining a constant ethylene pressure. After consuming a certain volume ethylene, the oligomerisation was stopped by rapid venting of the ethylene, decanting the product mixture into a collection bottle using a tap in the base of the autoclave. Exposure of the mixture to air resulted in rapid deactivation of the catalyst.

After addition of n-hexylbenzene (0.5-3.5 g) as internal standard to the crude product the amount of C_4 - C_{30} olefins was determined by gas chromatography, from which the (apparent) Schulz-Flory K(linear)-factor was determined by regression analysis, generally using the C_{10}-C_{28} data of the linear alpha olefins. By "apparent" is meant in the case that there is a small deviation from a Schulz-Flory distribution. In the ethene/1-octene co-oligomerisation, the 1-octene content was calculated from the regression analysis of the linear alpha olefins in the C_{10}-C_{28} range. In the ethene/1-hexadecene co-oligomerisation, the 1-hexadecene content was calculated from the regression analysis of the linear alpha olefins in the C_{18}-C_{28} range. The data are reported in Table 1.

The amount of solids in the product was determined as follows. The crude reaction product was centrifuged at 4000 rpm for 30 min after which the clear upper layer was decanted. The lower layer consisting of solid olefins, toluene and a minor amount of liquid olefins was mixed with 500 ml acetone using a high-shear mixer (Ultra-Turrax, type TP 18-10). The mixture was centrifuged under the above-mentioned conditions. The lower layer was mixed with 200 ml acetone and filtered off over a glass filter (porosity P3). The solid product was dried for 24 hours at 70 °C at <1kPa, weighed and its $<C_{32}$ contents determined by gas chromatography of a 1,2-dichlorobenzene or a 1,2,4-trichlorobenzene solution of the solids. The amounts of solids reported in Table 1 are the isolated solids having a carbon number $>C_{30}$.

The relative amounts of the linear (lin.) 1-hexene amongst all hexene isomers and the relative amount of the linear (lin.) 1-dodecene amongst all dodecene isomers

were evaluated by GC analysis and are reported in Table 1.

The yields of the branched C_{10}-C_{30} alpha olefins in case of ethene/1-octene co-oligomerisation, or the branched C_{18}-C_{30} alpha olefins in case of ethene/1-hexadecene co-oligomerisation, and the yields of the odd linear and branched C_9-C_{29} alpha olefins in the case of co-oligomerisation of ethene and 1-heptene were obtained by GC analysis. K(linear)-factors and/or K(branched)-factors were determined accordingly by regression analysis. These data are given in Table 1 and/or in the detailed description of the experiments.

The weight ratio of alkyl-branched 1-undecene(s) over alkyl-branched and linear 1-undecenes, the weight ratio of alkyl-branched 1-dodecene(s) over alkyl-branched and linear 1-dodecenes and the weight ratio of alkyl-branched 1-eicocene(s) over alkyl-branched and linear 1-eicocenes determined by GC analysis are reported in Table 1.

Example 1

Iron complex 3, pre-activated in the manner described in the "Catalyst System Preparation", was employed in a 1-litre steel autoclave, loaded with 0.5 g MAO and toluene (total volume 310 ml), in an ethylene oligomerisation experiment at 1.6 MPa ethylene pressure. After an ethylene consumption of 118.2 g the reaction was stopped, giving rise to 110.6 g of linear C_4-C_{30} alpha olefins and 2.5 g of solids $>C_{30}$. The total amount of ethylene oligomerisation product 113.1 g is slightly less than the ethylene uptake, which is attributed to loss of part of the volatile 1-butene and the formation small amounts of by-products.

The linear alpha olefins showed an almost perfect Schulz-Flory (S-F) distribution with K-factor of 0.72, as derived from regression analysis using the C_{10} - C_{28} contents, determined by GC (Regression statistics: R^2 = 1.00; standard error = 0.01 from 10 observations).

The Turn Over Frequency (T.O.F.) was 4.65E+07 mol ethylene/mol Fe*h.

The (linear) 1-hexene and 1-dodecene purity were 99.5 and 97.7% wt, respectively. The amounts of branched C_{12} alpha olefin and branched C_{20} alpha olefin were <2 and <3 % wt, respectively.

The details of Example 1 are given in Table 1.

Example 2

Example 2 is a repeat of Example 1 apart from the fact that part of the toluene has been replaced by 1-heptene. The ethylene uptake of 118.3 g resulted in 110.3 g even-numbered linear C_4-C_{30} alpha olefins, whilst 2.0 g solids >C_{30} were isolated. Besides these products GC analyses showed formation distributions of odd-numbered linear and branched alpha olefins. The odd (C_9-C_{29}) linear alpha olefins amounted to 1.7 g, whilst the odd branched alpha olefins amounted to 1.1 g.

The linear C_{10}-C_{28} alpha olefins showed a Schulz-Flory distribution, as derived from regression analysis, with a K(even-linear)-factor of 0.69 (R^2 = 1.00; standard error < 0.01 for 10 observations). Regression analysis of the odd-numbered linear C_9-C_{21} alpha olefins and the odd-numbered branched C_9-C_{21} alpha olefins gave Schulz-Flory distributions, having a K(odd-linear) of 0.70 (R^2 = 1.00; standard error = 0.02 for 7 observations) and a K(odd-

branched) of 0.68 (R^2 = 1.00; standard error = 0.02 for 7 observations), respectively.

The T.O.F. was 2.13E+07 mol ethylene/mol Fe*h.

The linear (lin.) 1-hexene and 1-dodecene purity were 99.0 and 96.1 % wt, respectively.

The details of Example 2 are given in Table 1.

Example 3

Example 3 was a repeat of Example 2, but with the 1-heptene replaced by a 1-octene. After an ethylene consumption of 118.0 g the reaction was stopped, giving rise to 125.4 g of linear C_4-C_{30} alpha olefins and 9.7 g of solids $>C_{30}$. The excess of linear alpha olefin production is attributed to incorporation of starting 1-octene in the final products as shown in Example 2.

The linear alpha olefins had a Schulz-Flory distribution with K-factor of 0.73, as derived from regression analysis using the C_{10} - C_{28} contents, determined by GC (Regression statistics: R^2 = 1.00; standard error = 0.02 from 10 observations).

The T.O.F. was 3.43E+07 mol ethylene/mol Fe*h.

The linear 1-hexene and linear 1-dodecene purity were 99.5 and 91.9 % wt, respectively.

GC and NMR data showed the by-products to be mainly methyl-branched (Me-branched) alpha olefins having a K-factor of 0.71 (R^2 = 0.98; standard error = 0.06 from 10 observations).

Details of the reaction are provided in Table 1.

Example 4

Example 4 is a repeat of Example 3, but now using 1-hexadecene instead of 1-octene. The amount of linear alpha-olefins was in excess of the amount of ethylene consumed: 116.3 *vs.* 111.5 g, respectively. The linear

alpha olefins had a Schulz-Flory distribution with K-factor of 0.72, as derived from regression analysis using the C_{18} - C_{28} contents, determined by GC (Regression statistics: R^2 = 1.00; standard error = 0.01 from 6 observations), as shown in Figure 1. It is clear from this Figure that 1,2-insertion of 1-hexadecene occurs, as confirmed by Example 2.

The T.O.F. was 1.42E+06 mol ethylene/mol Fe*h.

The linear 1-hexene and 1-dodecene purity were 99.6 and 97.9 % wt. The amount of alkyl-branched C_{20} alpha olefin was 11 % wt, whereas <3 % wt is observed in the absence of 1-hexadecene monomer, see Example 1.

GC and NMR data showed the by-products to be mainly methyl-branched alpha olefins having a K-factor of 0.70 (R^2 = 0.99; standard error = 0.04 from 6 observations).

Details of the reaction are provided in Table 1.

Example 5

Example 5 is a repeat of Example 2, but now at a higher 1-heptene concentration and a lower ethylene pressure of 0.7 MPa illustrating the effect of changing olefin concentrations. Besides even-numbered linear alpha olefins GC analyses showed formation distributions of odd-numbered linear and branched alpha olefins (see Figure 2 for the GC-trace). The odd (C_9-C_{29}) linear alpha olefins amounted to 11.9 g, whilst the odd methyl-branched alpha olefins amounted to 6.6 g.

The linear C_{10}-C_{28} alpha olefins showed a Schulz-Flory distribution, as derived from regression analysis, with a K(even-linear)-factor of 0.64 (R^2 = 1.00; standard error < 0.01 for 10 observations). Regression analysis of the odd-numbered linear C_9-C_{29} alpha olefins and the odd-

numbered methyl-branched C_9-C_{29} alpha olefins gave Schulz-Flory distributions, having a K(odd-linear) of 0.64 (R^2 = 1.00; standard error = 0.01 for 11 observations) and a K(odd-branched) of 0.63 (R^2 = 1.00; standard error = 0.03 for 11 observations), respectively.

Further details are provided in Table 1.

Example 6

Example 6 is a repeat of Example 3, but at different ethylene pressure of 0.7 MPa, demonstrating the effect of changing the olefin concentration. After an ethylene consumption of 68.8 g the reaction was stopped, giving rise to 85.8 g of linear C_4-C_{30} alpha olefins and 3.6 g of solids $>C_{30}$. The excess of linear alpha olefin production is attributed to incorporation of starting 1-octene in the final products as shown in Examples 2, 4 and 5.

The linear alpha olefins had a Schulz-Flory distribution with K-factor of 0.70, as derived from regression analysis using the C_{10} - C_{28} contents, determined by GC (Regression statistics: R^2 = 1.00; standard error = 0.02 from 10 observations).

The T.O.F. was 1.10E+07 mol ethylene/mol Fe*h.

The linear 1-hexene and linear 1-dodecene purity were 99.2 and 84.7 % wt, respectively. GC and NMR data showed the by-products to be mainly methyl-branched alpha olefins having a K-factor of 0.70 (R^2 = 1.00; standard error = 0.04 from 10 observations).

Details of the reactions and products are given in Table 1.

Example 7

Example 7 is a repeat of Example 6, but at different 1-octene concentration, demonstrating the effect of changing the olefin concentration. The results are similar to those of Example 6. Details of the reactions and products are given in Table 1.

The following series of experiments demonstrate the effects of catalyst systems with different bis-iminepyridine ligands.

Example 8

Iron complex X (prepared according to WO-A-99/02472) was employed in a reaction nearly identical to Example 6. The yield of linear alpha olefins in the C_4-C_{30} range of was 96.9 g, which is in excess of the ethylene consumption of 68.7 g, which is indicative of 1-octene incorporation in the products.

The linear 1-hexene purity was 98.0 % wt and the alkyl-branched 1-dodecene content was 14 % wt. GC and NMR data showed the by-products to be mainly methyl- and ethyl-branched (Me- and Et-branched) alpha olefins in a ratio of about 1 : 1. Details of the reaction are provided in Table 1.

Example 9

Iron complex 5 was employed in an 1-octene co-oligomerisation experiment at 0.7 MPa ethylene pressure under conditions similar to that of Example 7. The yield of linear alpha olefins in the C_4-C_{30} range of 60.2 g is in excess of the ethylene consumption of 53.5 g.

The linear 1-hexene purity was 94.7 % wt and the alkyl-branched 1-dodecene content was 28 % wt. GC and NMR data showed the by-products to be mainly methyl- and ethyl-branched alpha olefins in a ratio of approximately

1:1 (see Figure 3 for GC-trace wherein A is vinylidene olefin, B is internal olefins, C and D are ethyl branched olefins). Details of the reaction are provided in Table 1.

Example 10

Example 10 is a repeat of Example 9, but now using iron complex 5'. The results are similar to those of Example 9. Details are provided in Table 1.

Example 11

Iron complex 8 was employed in 1-octene co-oligomerisation experiment almost identical to that of Example 7. The yield of linear alpha olefins in the C_4-C_{30} range was 73.6 g which is in excess of the ethylene consumption of 68.6 g.

Linearity of 1-hexene fraction was 96.8 % wt and alkyl-branched 1-dodecene content was 20 % wt. GC and NMR data showed the by-products to be mainly methyl- and ethyl-branched alpha olefins in a ratio of approximately 1:1. Details of the reaction are provided in Table 1.

Example 12

Iron complex 11 was employed in 1-octene co-oligomerisation experiment nearly identical to that of Example 7. The total yield of products was >75.6 g, in excess of ethylene consumption of 68.8 g. The linear 1-hexene purity was 99.2 % wt and alkyl-branched 1-dodecene content was 5 % wt. GC and NMR data showed the by-products to be mainly methyl-branched alpha olefins. Details of the reaction are provided in Table 1.

Example 13

Iron complex 13 was employed in 1-octene co-oligomerisation experiment under conditions similar to that of Example 7. The linear 1-hexene purity was 98.8 % wt and the alkyl-branched 1-dodecene content was 4 % wt.

GC and NMR data showed the by-products to be mainly methyl-branched alpha olefins. Details of the reaction are provided in Table 1.

Example 14

Iron complex 15 was employed in 1-octene co-oligomerisation experiment under conditions almost identical to that of Example 6. The linear 1-hexene purity was 99.1 % wt and the alkyl-branched 1-dodecene content was 16 % wt. GC and NMR data showed the by-products to be mainly methyl-branched alpha olefins. Details of the reaction are provided in Table 1.

Example 15

Iron complex 17 was employed in 1-octene co-oligomerisation experiment under conditions almost identical to those of Example 7. The yield of linear alpha olefins in the C_4-C_{30} range was 69.5 g which is in excess of the ethylene consumption of 49.8 g. The linear 1-hexene purity was 98.4 % wt and the alkyl-branched 1-dodecene content was 17 % wt. GC and NMR data showed the by-products to be mainly methyl- and ethyl-branched alpha olefins in a ratio of about 1:1. Details of the reaction are provided in Table 1.

Example 16

Iron complex 20 was employed in 1-octene co-oligomerisation experiment under conditions almost identical to those of Example 6. The linear 1-hexene purity was 97.8 % wt and the alkyl-branched 1-dodecene content was 21 % wt. GC and NMR data showed the by-products to be mainly Me- and Et-branched alpha olefins in a ratio of about 1 : 1. Details of the reaction are provided in Table 1.

Example 17

Iron complex 22 was used in a 1-octene oligomerisation experiment under conditions almost identical to those of Example 6. The K-factor was very low, implying that much of the ethylene is converted into 1-butene, which takes part in the co-oligomerisation. This is reflected by the purity of 1-hexene of 54.4 % wt. The remainder are largely branched hexenes. The branched 1-dodecene content was 33 % wt. GC indicated the by-products to be mainly Me- and Et-branched alpha olefins in a ratio of about 1 : 1. Details of the reaction are provided in Table 1.

TABLE 1

Example Number	Ex.1	Ex.2[1]	Ex.3	Ex.4[2]	Ex.5[1]	Ex.6	Ex.7
Iron Complex/ (Intake in nmol)	3 (215)	3 (518)	3 (225)	3 (2166)	3 (3150)	3 (198)	3 (507)
[Al]/[Fe] (mol/mol)	4600	2100	4400	2100	650	5000	2200
Reaction Time (min)	25	23	33	78	40	68	43
Ethene Pressure (MPa)	1.6	1.6	1.6	1.6	0.7	0.7	0.7
Toluene intake (ml)	310	290	60	150	230	60	90
1-Octene intake (ml)	0	34[1]	260	250[2]	260[1]	262	256
Ethene consumed (g)	118.2	118.3	118.0	111.5	68.8	68.8	68.7
Linear Product <C32 (g)	110.6	110.3[3] 1.7[4]	125.4	116.3	57.6[3] 11.9[4]	85.8	79.7
Branched Product <C32 (g)	n.d.	1.1[4]	5.5	2.2	6.6[4]	8.7	9.3
Isolated Solids >C30 (g)	2.5	2.0	9.7	7.3	0.3	3.6	2.4
T.O.F. (molC2=/ molFe*h)	4.65 E+07	2.13 E+07	3.43 E+07	1.42 E+06	1.16 E+06	1.10 E+07	6.67 E+06
K(linear)	0.72	0.69[3] 0.70[4]	0.73	0.72	0.64[3] 0.64[4]	0.70	0.69
Lin.1-C_6= purity (%wt)	99.5	99.0	99.5	99.6	99.0	99.2	99.1
Lin.1-C_{12}= purity (%wt)	97.7	96.1	91.9	97.9	98.0	84.7	83.3
K(branch)	n.d.	0.68	0.71	0.70	0.63	0.70	0.70
Branched 1-C_{12}= (%wt)	<2	40[6]	7	11[5]	38[6]	14	15

TABLE 1 (continued)

Example Number	Ex.8[7]	Ex.9	Ex.10	Ex.11	Ex.12	Ex.13	Ex.14
Iron Complex/ (Intake in nmol)	X[7] (562)	5 (1920)	5' (1780)	8 (3510)	11 (2540)	13 (3170)	15 (672)
[Al]/[Fe] (mol/mol)	1900	900	900	600	700	600	1700
Reaction Time (min)	18	69	74	59	58	62	20
Ethene Pressure (MPa)	0.7	0.7	0.7	0.7	0.7	0.7	0.7
Toluene intake (ml)	60	120	90	90	90	150	60
1-Octene intake (ml)	247	243	230	254	242	261	260
Ethene consumed (g)	68.7	53.5	80.4	68.6	68.8	33.6	68.4
Linear Product <C32 (g)	96.9	60.2	91.5	73.6	55.1	29.1	49.4
Isolated Solids >C30 (g)	5.9	<0.1	<0.1	7.6	20.5	11.7	9.0
T.O.F. (molC2=/ molFe*h)	1.44 E+07	8.70 E+05	1.31 E+06	7.12 E+05	1.00 E+06	3.66 E+05	1.11 E+07
K(linear)	0.70	0.46	0.44	0.73	0.82	0.82	0.76
Lin.1-C_6= purity (%wt)	98.0	94.7	92.5	96.8	99.2	98.8	99.1
Lin.1-C_{12}= purity (%wt)	82.0	66.3	65.5	75.9	94.3	94.9	82.6
Branched 1-C_{12}= (%wt)	14	28	29	20	5	4	16

TABLE 1 (continued)

Example Number	Ex. 15	Ex. 16	Ex. 17
Iron Complex/ (Intake in nmol)	17 (353)	20 (984)	22 (4230)
[Al]/[Fe] (mol/mol)	2900	1300	600
Reaction Time (min)	42	59	45
Ethene Pressure (MPa)	0.7	0.7	0.7
Toluene intake (ml)	90	60	60
1-Octene intake (ml)	255	234	237
Ethene consumed (g)	49.8	42.2	64.8
Linear Product <C32 (g)	69.5	65.0	30.8
Isolated Solids >C30 (g)	2.1	1.5	<0.1
T.O.F. (molC2=/ molFe*h)	7.19 E+06	1.54 E+06	5.47 E+05
K(linear)	0.66	0.59	0.2
Lin.1-C_6= purity (%wt)	98.5	97.8	54.4
Lin.1-C_{12}= purity (%wt)	79.4	75.2	61.1
Branched 1-C_{12}= (%wt)	17	21	33

Experiments carried out at 70°C in 1-octene/toluene, using 1-litre steel autoclave, unless indicated otherwise.

n.d. = not determined.

[1] 1-Heptene used instead of 1-octene.

[2] 1-Hexadecene used instead of 1-octene.

[3] Refers to even-numbered alpha olefins.

[4] Refers to odd-numbered alpha olefins.

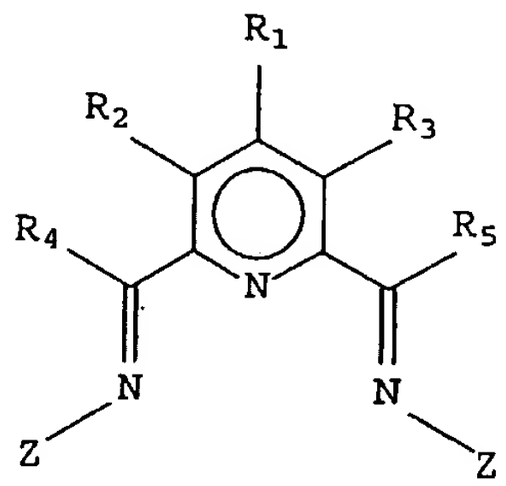
[5] Weight ratio of alkyl-branched 1-C_{20}= over alkyl-branched and linear 1-C_{20}=, in % wt.

[6] Weight ratio of alkyl-branched 1-C_{11}= over alkyl-branched and linear 1-C_{11}=, in % wt.

[7] Catalyst prepared according to WO-A-99/02472.

C L A I M S

1. A process for production of higher linear alpha olefins and/or alkyl-branched alpha olefins, which comprises the co-oligomerisation of one or more alpha olefins with ethylene in the presence of a metal catalyst system employing one or more bis-aryliminepyridine MX_a complexes and/or one or more [bis-aryliminepyridine $MY_p.L_b^+][NC^-]_q$ complexes, said bis-aryliminepyridine complexes comprising a ligand of the formula,

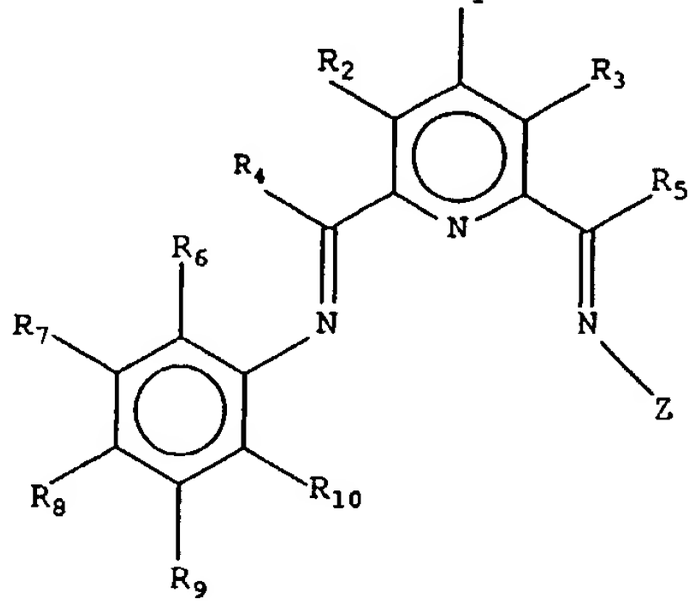


(I)

wherein M is a metal atom selected from Fe or Co; a is 2 or 3; X is halide, optionally substituted hydrocarbyl, alkoxide, amide, or hydride; Y is a ligand which may insert an olefin; NC^- is a non-coordinating anion; p+q is 2 or 3, matching the formal oxidation of said metal atom; L is a neutral Lewis donor molecule; b = 0, 1, or 2; R_1-R_5 are each, independently, hydrogen, optionally substituted hydrocarbyl, an inert functional group, or any two of R_1-R_3 vicinal to one another taken together may form a ring; each Z, which may be identical or different, is an optionally substituted aromatic

hydrocarbon ring; an optionally substituted polyaromatic hydrocarbon moiety; an optionally substituted heterohydrocarbyl moiety; or an optionally substituted aromatic hydrocarbon ring in combination with a metal, said optionally substituted aromatic hydrocarbon ring being π-co-ordinated to the metal; and said process is carried out at an ethylene pressure of less than 2.5 MPa.

2. A process according to Claim 1, wherein said ligand is of the formula,

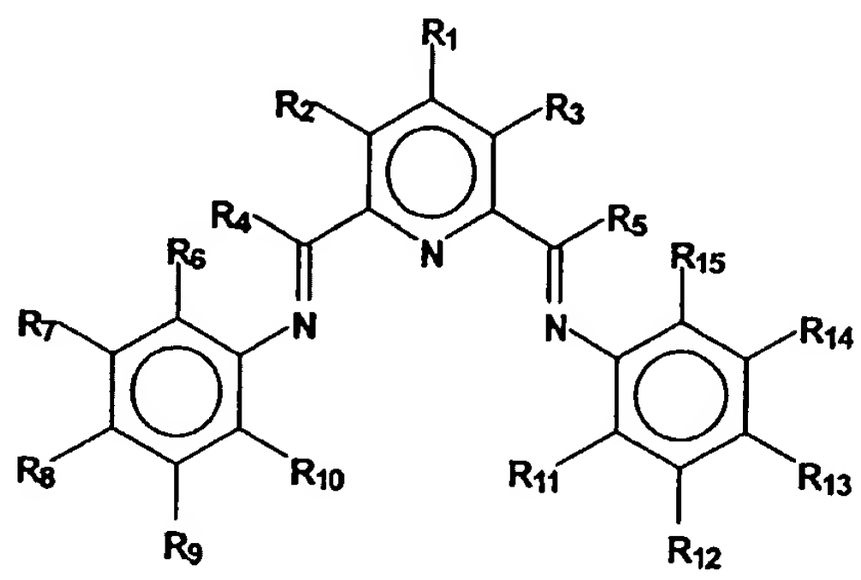


(II)

wherein R_1-R_{10} are each, independently, hydrogen, optionally substituted hydrocarbyl, an inert functional group, or any two of R_1-R_3, R_6-R_{10} vicinal to one another taken together may form a ring; R_6 may be taken together with R_4 to form a ring; R_{10} may be taken together with R_4 to form a ring; Z is an optionally substituted aromatic hydrocarbon ring; an optionally substituted polyaromatic hydrocarbon moiety; an optionally substituted heterohydrocarbyl moiety; or an optionally substituted aromatic hydrocarbon ring in combination with a metal,

said optionally substituted aromatic hydrocarbon ring being π-co-ordinated to the metal.

3. A process according to Claim 1 or 2, wherein said ligand is of the formula,



(III)

wherein R_1-R_5, R_7-R_9 and R_{12}-R_{14} are each, independently, hydrogen, optionally substituted hydrocarbyl, an inert functional group, or any two of R_1-R_3, R_7-R_9 and R_{12}-R_{14} vicinal to one another taken together may form a ring; R_6 is hydrogen, optionally substituted hydrocarbyl, an inert functional group, or taken together with R_7 or R_4 to form a ring; R_{10} is hydrogen, optionally substituted hydrocarbyl, an inert functional group, or taken together with R_9 or R_4 to form a ring; R_{11} is hydrogen, optionally substituted hydrocarbyl, an inert functional group, or taken together with R_5 or R_{12} to form a ring; and R_{15} is hydrogen, optionally substituted hydrocarbyl, an inert functional group, or taken together with R_5 or R_{14} to form a ring.

4. A process according to Claim 3, wherein R_1-R_5, R_7-R_9 and R_{12}-R_{14} are each, independently, hydrogen, optionally substituted hydrocarbyl, an inert functional group, or any two of R_1-R_3, R_7-R_9 and R_{12}-R_{14} vicinal to one another taken together may form a ring; R_6 is a primary carbon group, a secondary carbon group or a tertiary carbon group; and provided that:

when R_6 is a primary carbon group none, one or two of R_{10}, R_{11} and R_{15} are primary carbon groups, and the remainder of R_{10}, R_{11} and R_{15} are hydrogen;

when R_6 is a secondary carbon group none or one of R_{10}, R_{11} and R_{15} is a primary carbon group or a secondary carbon group and the remainder of R_{10}, R_{11} and R_{15} are hydrogen;

when R_6 is a tertiary carbon group all of R_{10}, R_{11} and R_{15} are hydrogen; and

any two of R_6, R_7, R_8, R_9, R_{10}, R_{11}, R_{12}, R_{13}, R_{14} and R_{15} vicinal to one another, taken together may form a ring.

5. A process according to Claim 3, wherein R_1-R_5, R_7-R_9 and R_{12}-R_{14} are each, independently, hydrogen, optionally substituted hydrocarbyl, an inert functional group, or any two of R_1-R_3, R_7-R_9 and R_{12}-R_{14} vicinal to one another taken together may form a ring; R_6 is hydrogen, optionally substituted hydrocarbyl, an inert functional group, or taken together with R_7 or R_4 to form a ring;

R_{10} is hydrogen, optionally substituted hydrocarbyl, an inert functional group, or taken together with R_9 or R_4 to form a ring; R_{11} and R_{15} are, independently, hydrogen or an inert functional group.

6. A process according to Claim 3, wherein R_1-R_5, R_7-R_9 and R_{12}-R_{14} are each, independently, hydrogen, optionally substituted hydrocarbyl, an inert functional group, or any two of R_1-R_3, R_7-R_9 and R_{12}-R_{14} vicinal to one another taken together may form a ring; R_6, R_{10}, R_{11} and R_{15} are identical and are each selected from fluorine or chlorine.

7. A process according to any one of Claims 1 to 6, wherein alpha olefin co-monomer is generally present in a concentration of greater than 1 $mol.l^{-1}$.

8. A composition comprising linear alpha olefins and/or alkyl branched alpha olefins produced according to the process of any one of Claims 1 to 7.

9. A composition comprising linear alpha olefins and/or alkyl-branched alpha olefins, wherein said composition contains greater than 5 % wt. alkyl-branched alpha olefins based on the total weight of linear alpha olefins and alkyl-branched alpha olefins in the product composition.

10. A composition according to Claim 8 or 9, wherein said alkyl-branched alpha olefins are methyl- and/or ethyl-branched alpha olefins.

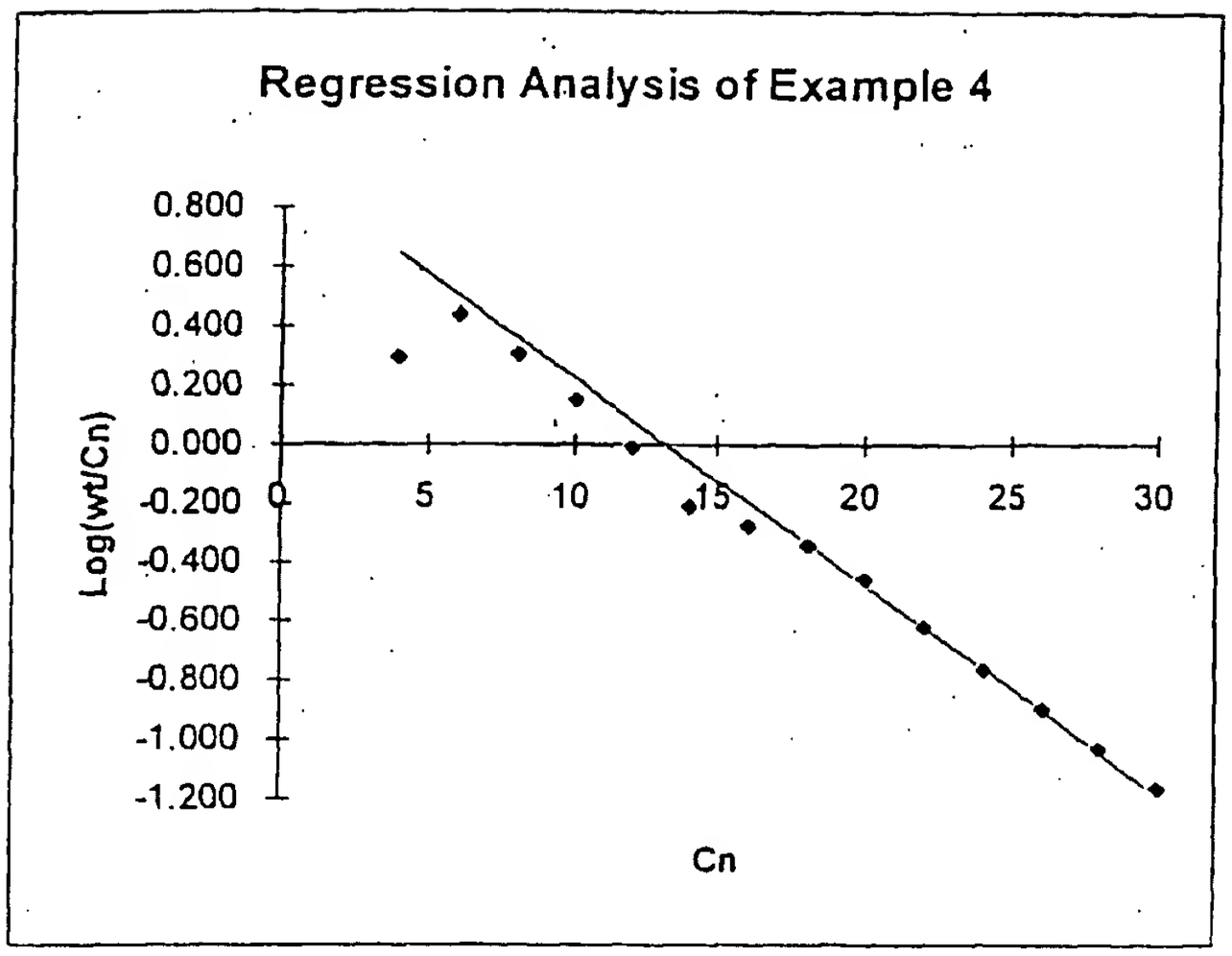


Figure 1: Regression Analysis of Example 4

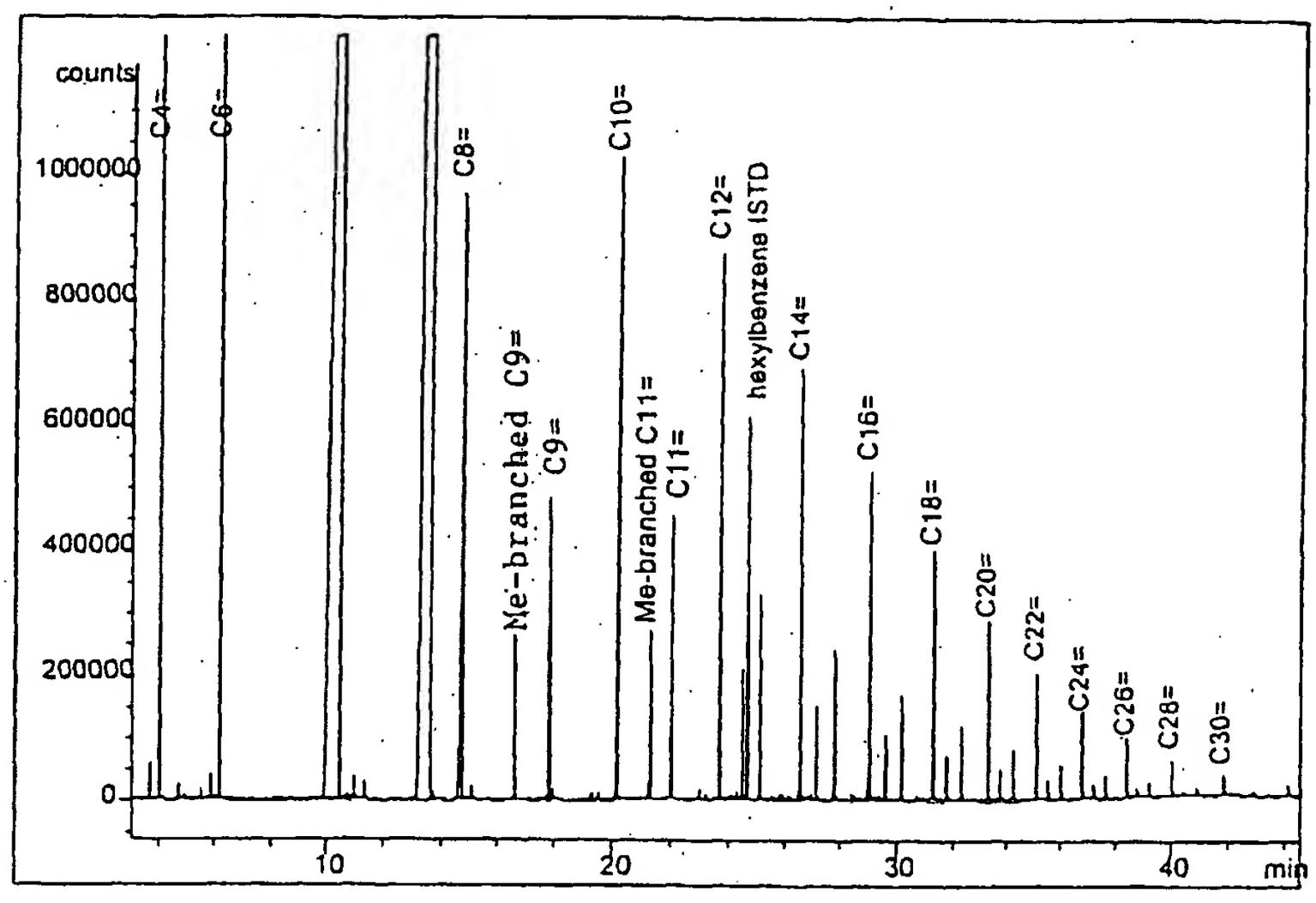


Figure 2: GC-trace of product of Example 5

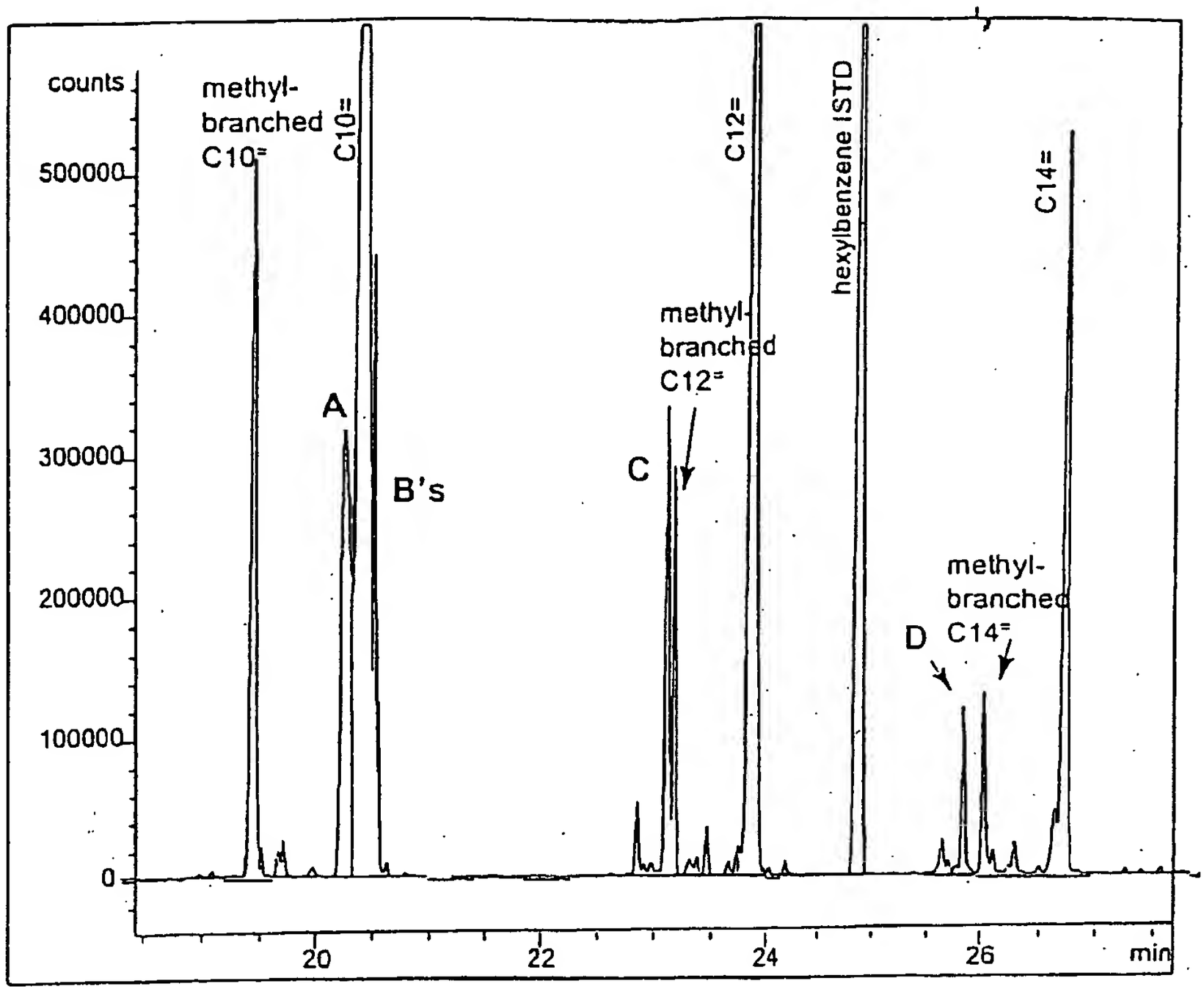


Figure 3: GC-trace (in part) of product of Example 9

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WO 02/028805 A3

(54) Title: PROCESS FOR THE CO-OLIGOMERISATION OF ETHYLENE AND ALPHA OLEFINS

(57) Abstract: A process for production of higher linear alpha olefins and/or alkyl-branched alpha olefins, which comprises the co-oligomerisation of one or more alpha olefins with ethylene in the presence of a metal catalyst system employing one or more bis-aryliminepyridine MX_a complexes and/or one or more [bis-aryliminepyridine $MY_P.L_b^+$] $[NC^-]_q$ complexes; and said process is carried out at an ethylene pressure of less than 2.5 MPa.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 01/11392

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C2/32 C07C11/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 02472 A (E. I. DU PONT DE NEMOURS; UNIVERSITY OF NORTH CAROLINA AT CHAPEL HILL) 21 January 1999 (1999-01-21) cited in the application claims	1-8
X	WO 99 51550 A (E. I. DU PONT DE NEMOURS) 14 October 1999 (1999-10-14) claims	1-8

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the International search	Date of mailing of the international search report
18 April 2002	03. 05. 2002

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Van Geyt, J

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP 01/11392

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 9-10(in part)
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-8, 10 (in part)

A process for production of higher alpha olefins and/or alkyl-branched alpha olefins by co-oligomerisation of alpha olefins and ethylene and the compositions prepared by this process

2. Claims: 9(complete),10(in part)

A composition comprising linear alpha olefins and/or alkyl-branched alpha olefins

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 01/11392

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		CN 1296466 T	23-05-2001
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